THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. L SEPTEMBER 1955 No. 9

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SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
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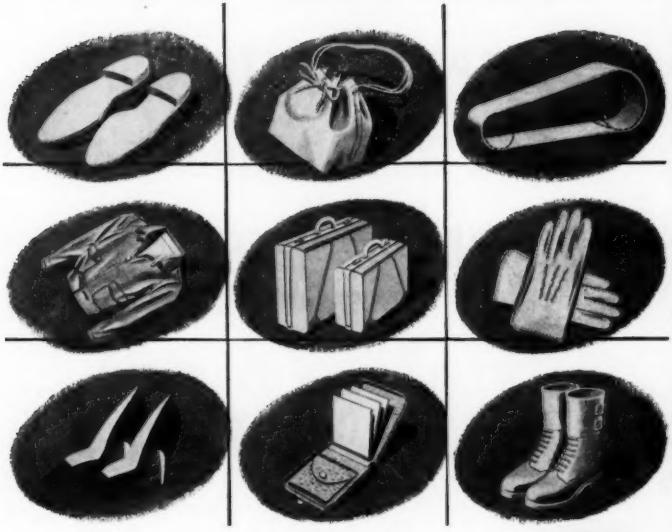

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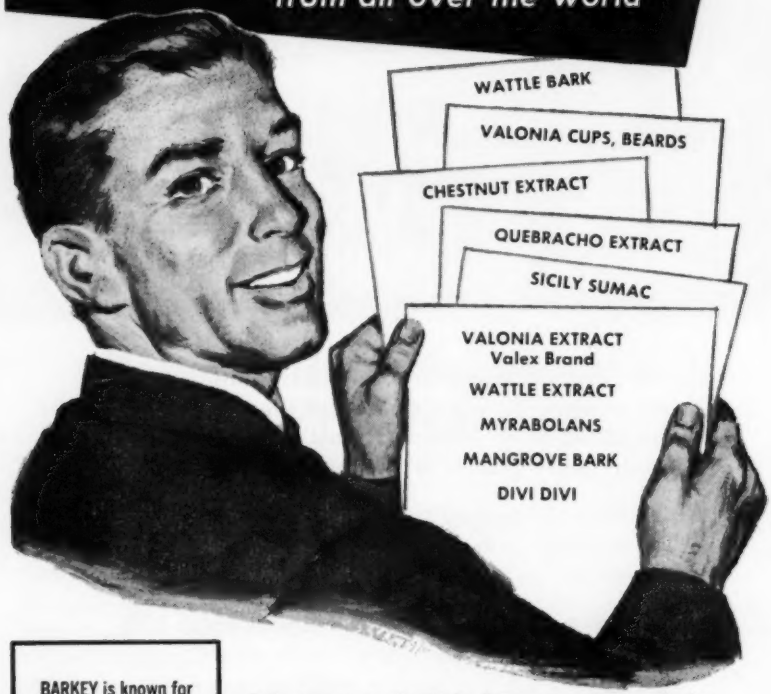

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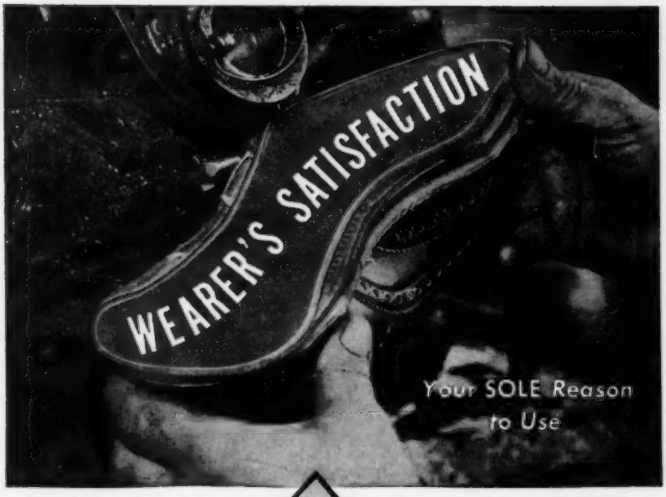

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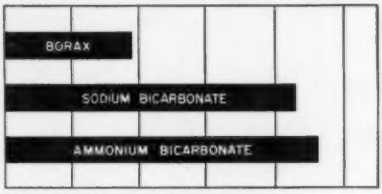
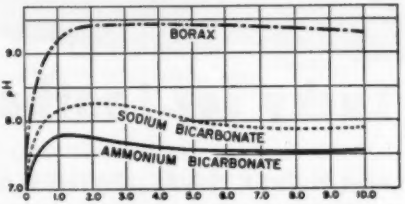


Pounds of hydrochloric acid neutralized by 1 lb. of alkali

2. Lower pH



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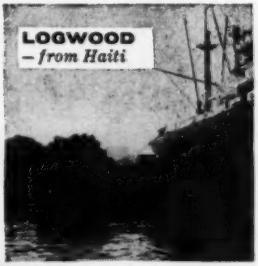

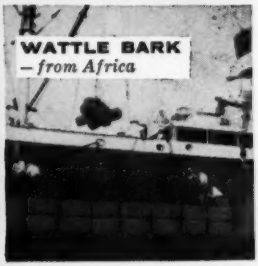

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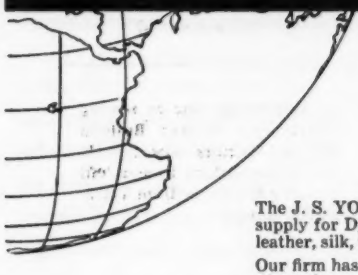

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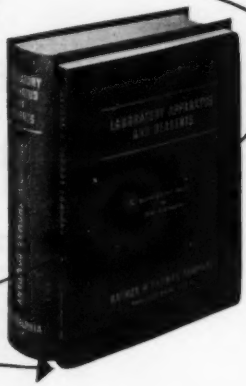

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Vol. L SEPTEMBER 1955 No. 9

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Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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DEAN WILLIAMS—OBITUARY

Robert Perry Dean Williams, Editor of the Journal, died suddenly, Sunday, August 14th at 4:00 p. m. in the afternoon at the Potter County Memorial Hospital in Coudersport, Pennsylvania. Funeral services and interment were at Ridgway, Pennsylvania on August 17th.

Dean Williams was born July 11, 1891 at Reynoldsville, the son of John Calvin and Permelia Adel Dean Williams. Dean Williams married Wilma Elizabeth Chamberlin in 1918 and is survived by his widow and three sons.

Dean Williams received his professional degree from Pennsylvania State College and after a brief period with the Clawson Chemical Company, he joined the United States Leather Company where he became Vice President in charge of production. Since 1950 he has been affiliated with L. H. Lincoln and Son, Inc., Coudersport, Pennsylvania where he was Vice President.

Mr. Williams was Associate Editor of the Journal for 13 years, 1923 to 1936 and Editor for 19 years, 1936 to 1955, a total of 32 years of intimate association with the Journal. Mr. Williams saw the Journal become the outstanding Journal in Leather Technology in the world.

Dean Williams held many important responsibilities in the field of Leather Technology. He was past president of the American Leather Chemists' Association and the recipient of the Alsop award for outstanding contributions to the tanning and leather industry.

Dean Williams was a member of the American Chemical Society, The Society of Chemical Industry, the International Society of Leather Chemists, a member of the Chemist's Club of New York. He was a member of the First Presbyterian Church of Ridgway and a 32 Degree Mason.

The passing of Dean Williams has brought sorrow to his great host of friends and associates and the sympathy of all is extended to the surviving family.

FRED O'FLAHERTY

BUREAU OF EMPLOYMENT

"Tannery Chemist desires position in progressive tannery. Twenty-two years experience in chemistry. Specializing in all phases of tannery control. Vegetable and chrome liquor, paste and paste unit control. Reply to Box NH184, c/o Secretary of A.L.C.A., University of Cincinnati, Cincinnati 21, Ohio."

A Swedish tanner, 48 years old, with experience in all types of leather, wishes a position as tanner in the United States. Address replies to Eric Jonsson, Garmisch-Partenkirchen, 52 Meximilianstr., Garmische, West-Germany.

MINUTES OF MEETING OF THE STANDARDS AND SPECIFICATIONS COMMITTEE

NEW OCEAN HOUSE, SWAMPSCOTT, MASS.

MAY 22nd, 1955

The meeting convened at 5:00 P. M., with the following members present: R. G. Ashcraft, M. H. Battles, G. A. Brown, S. Dahl, K. H. Knight, R. M. Lollar, C. W. Mann, R. L. Young, and C. G. Telander, *Chairman*. Guest: J. R. Kanagy.

The Chairman reviewed the subjects discussed and actions taken by the Committee since the last report of May 1954, as follows:

During the period May 1954—May 1955, the following Proposed Revisions of Federal Leather Specifications were presented to the Committee for comments and approval:

KK-L-154a,	Bag and Case Leather.
KK-L-00167a,	Chamois, Revision No. 2.
KK-L-311a,	Method 2211, Resistance to Grain Cracking.
KK-L-311a,	Methods 1011, 1111, 1121, 1211, Sampling.
KK-L-311a,	Methods 6211, 6221, Moisture Determinations.
KK-L-271c,	Strap Leather.
KK-L-170,	Amendment No. 1, Goatskin, Chrome Tanned.
KK-W-231a,	Welting.
KK-L-00181c,	Hydraulic Packing, Vegetable Tanned.
KK-L-00177c,	Hydraulic Packing, Mineral Tanned.
KK-L-00201c,	Lace Leather.
KK-B-00201c,	Belting, Flat, Vegetable Tanned.
KK-L-00171d,	Harness, Vegetable Tanned.
KK-L-00169a,	Horsehide.
KK-L-00291d,	Upholstery.
KK-L-00261d,	Sole Leather, Sampling on Area versus Weight Basis.

Sampling of Cut Stock to avoid "edge effect" in conjunction with KK-L-191 Incoles, and MIL-11636b, Insoles.

In most instances the Proposed Revisions were approved by the Committee with only minor changes recommended. In judging Specification KK-L-00177c, Hydraulic Packing, Mineral Tanned, the assistance of the manufacturers of this item was sought and suggestion made for changes in specification limits.

Action on KK-L-00261d and Methods 6211, 6221 of KK-L-311a is pending at the time of the annual meeting.

The Committee approved this review and the actions taken during the past year.

Methods 6211 and 6221 of KK-L-311a, Moisture Determination, were referred to the Committee on Vegetable Leathers. The question of area versus

weight compositing of sole leather in conjunction with the pending revision of KK-L-00261d, Sole Leather, was reviewed. In expressing their preference, seven members were in favor of area basis, two in favor of weight basis, and one member would permit both methods. Two members did not make any recommendation in the matter. The statistical evaluation of this question, made by J. R. Kanagy, R. M. Lollar and C. W. Mann, showed that no significant difference existed between area and weight compositing methods. The Chairman recommended that the evidence reviewed by the Committee be put into the form of a committee report to be published in the Journal for the sake of recording it; such report to be approved by the Committee before publication. Mr. C. W. Mann was appointed to prepare the material for publication. The Chairman was authorized to recommend to the Bureau of Standards Leather Section that sole leather samples should be composited on an equal area basis by the use of a die.

The duties of this Committee were reviewed. Both Tanners' Council and this Committee examine any proposed changes in leather specifications, and the Tanners' Council is in all cases informed of the recommendations by this Committee through Dr. Fred O'Flaherty. The Committee has at times considered questions concerning Federal Specifications for leather outside its scope, which is, strictly speaking, limited to methods of analysis and testing. Physical test methods have been referred to the Committee on Physical and Mechanical Properties. It was the concensus of opinion that direct numerical limits of specification requirements should not be recommended or endorsed by this Committee. Such matters requiring action on definite specification limits not caused by change in analysis or sampling methods should be referred to the industry through Tanners' Council.

The Chairman raised the question as to whether the Committee should consider quality standards for the leather industry. The membership present felt that the Federal Leather Specifications are sufficient and that they reflect adequately present day manufacturing standards.

A close examination of the precision of analytical methods for leather analyses would be very desirable so that eventually all analytical methods in the methods booklet could be designated with a given degree of reproducibility. This question was presented to the Committee by Dr. R. M. Lollar during the 1952 meeting, (See *This Journal*, **47**, 581, 1952). The matter was at that time referred to Council for consideration since the investigation necessary for complete coverage was outside the ability of the Committee to handle. The Committee recommended that the matter be again brought to the attention of the Council for assignment.

Metting adjourned at 6:30 P. M.

CARL G. TELANDER, *Chairman*

MISCELLANEOUS TANNERY MATERIALS—GENERAL (G-1)

1. SCOPE

1.1 These methods are intended for use in assaying various tannery chemicals.

2. SAMPLES

2.1 The preparation of a sample for analysis shall be as described in the given methods.

3. APPARATUS AND REAGENTS

3.1 All volumetric glassware used in the chemical analysis shall comply with specifications for Class B of Federal Specification DD-V-581, volumetric apparatus, glass.

3.2 Unless otherwise specified, all reagents used in the chemical analysis shall comply with specifications recommended by the committee on analytical reagents of the American Chemical Society.

3.3 General laboratory apparatus and reagents shall be available.

4. PROCEDURE

4.1 All dishes, flasks and other apparatus used during the analysis shall be covered with suitable covers so as to prevent, or reduce to a minimum, any change in concentration of solutions by evaporation of water.

4.2 All aliquots of analytical solutions, shall be measured at the same temperature.

5. GENERAL ANALYTICAL PROCEDURE FOR THE ASSAYING OF TANNERY CHEMICALS.

5.1 Miscellaneous Tannery Materials	(Method G2)
5.2 Egg Yolk	(Method G3)
5.3 Lactic Acid	(Method G4)
5.4 Oxalic Acid	(Method G5)
5.5 Tannery Sugars	(Method G6)

MISCELLANEOUS TANNERY MATERIALS (G-2)

The following chemicals listed as miscellaneous tannery materials can be assayed according to methods outlined in "Scott's Standard Methods of Chemical Analysis," Fifth Edition, 1939. N. Howell Furman, Editor. D.

Van Nostrand Co., Inc. New York, N. Y. or by methods outlined in "Reagent Chemicals and Standards." by Joseph Rosin, Third Edition, 1955. D. Van Nostrand Co., Inc., New York, N. Y.

Alum (Aluminum-ammonium sulfate and aluminum-potassium sulfate)
Ammonium chloride
Borax (Sodium borate)
Calcium formate
Calcium oxide
Epsom salts (Magnesium sulfate)
Lactic acid
Lime (see calcium oxide)
Magnesium sulfate
Oxalic acid
Sodium bicarbonate
Soda ash (Sodium carbonate)
Sodium bisulfite
Sodium borate
Sodium chloride
Sodium dichromate
Sodium formate
Sodium sulfate
Sodium sulfide
Sodium sulfite
Sulfuric acid

EGG YOLK (G-3)

1. SCOPE

1.1 This method is intended for the analysis of water, ash, sodium chloride, borates, fat, and albumin in assaying egg yolk.

2. APPARATUS AND REAGENTS

2.1 Platinum dish.
2.2 100 ml. volumetric flask.
2.3 Weighing bottle.
2.4 Soxhlet apparatus.
2.5 Kjeldahl flask.
2.6 Concentrated sulfuric acid.

2.7 Standardized 0.1 *N* hydrochloric acid.
2.8 Solution of methyl orange.
2.9 Concentrated hydrochloric acid.
2.10 Solution of phenolphthalein.
2.11 Standardized 0.1 *N* silver nitrate.
2.12 Potassium chromate indicator.
2.13 Tumeric paper.
2.14 Standardized 0.1 *N* sulfuric acid.
2.15 Standardized 0.5 *N* sodium hydroxide.
2.16 Neutral mannitol.
2.17 Chloroform.

3. PROCEDURE

3.1 Water. Weigh accurately about 5 g. of egg into a weighed platinum dish. Place in an oven at not over 105 °C. and heat over night. Cool for exactly 15 minutes in an individual desiccator over fresh concentrated sulfuric acid. Weigh as rapidly as possible, since the dried residue is very hydroscopic. Replace the dish in the oven for 1 hour, cool as before and reweigh. Repeat to constant weight. Take the loss in weight at 105 °C. as water.

3.2 Ash. Heat the residue obtained in the determination of water over a small flame until it is completely charred. Extract the charred mass with several 25 ml. portions of hot water, filter and collect the filtrate in a small beaker. Return the filter paper to the dish and ash the residue at dull red heat. This procedure is advisable because it is almost impossible to burn off all the carbon in the presence of much salt without heating so hot as to volatilize part of the salt. By the procedure given, most of the salt is removed from the material before final ignition. Evaporate the solution to a small bulk and transfer the residue quantitatively to the dish. Evaporate to dryness on the water bath, then heat at about 200 °C. for one hour. Cool in a desiccator and weigh.

(a) Sodium carbonate. Add exactly 10 ml. of 0.1 *N* hydrochloric acid to the ash and let stand for about 5 minutes. Add methyl orange indicator, and if the solution is not acid add 10 ml. more of 0.1 *N* hydrochloric acid. Rinse the solution into a beaker, dilute to about 100 ml. and titrate the excess acid with 0.1 *N*. sodium hydroxide.

(b) Iron and Aluminum. Treat the residue in the dish used for the determination of ash with about 5 ml. of concentrated hydrochloric acid, and heat nearly to boiling, add the solution to that in which sodium carbonate was titrated as described above, and filter if necessary. Precipitate with ammonia, filter, ignite and weigh iron and aluminum as oxides.

(c) Calcium. Precipitate calcium as oxalate in the filtrate from iron and alumnia and weigh as oxide.

3.3 Sodium Chloride. Weigh accurately about 1 g. of egg into a platinum dish and heat gently until all organic matter is carbonized, as described under (3.2). Take up the charred mass with hot water and filter. If the filtrate is colored, due to incomplete carbonization, reject the determination. Wash the residue on the filter paper until the solution passing through the filter no longer gives a precipitate on testing a few drops with silver nitrate solution. Combine the filtrate and washings, and add a few drops of phenolphthalein indicator. If the solution proves to be alkaline, acidify with dilute acetic acid. Add a few drops of potassium chromate indicator and titrate with 0.1 *N* silver nitrate solution until a brick-red precipitate forms.

3.4 Borates.

(a) Preliminary Test. Acidify the sample with hydrochloride acid in the proportion of 7 ml. of strong acid to 100 ml. of sample. In the case of solid or pasty samples heat with enough water to make sufficiently fluid before acidifying. Immerse a strip of tumeric paper in the acidified liquid and allow the paper to dry spontaneously. If borax or boric acid is present, the paper will acquire a characteristic red color, changing by strong ammonium hydroxide to dark blue green but restored by acid.

(b) Confirmatory Test. Make about 25 g. of the sample decidedly alkaline with lime water and evaporate to dryness on a steam bath. Ignite the dry residue at a low red heat until all organic matter is thoroughly charred, cool, digest with about 15 ml. of water, and add strong hydrochloric acid, drop by drop, until the solution is distinctly acid. Immerse a piece of turmeric paper in the solution and allow it to dry without heat. In the presence of borax or boric acid, the color will be the same as described under the preliminary test.

(c). Quantitative Method. Make 10 g. of the material distinctly alkaline with sodium hydroxide solution and evaporate to dryness in a platinum dish. Ignite the residue until the organic matter is thoroughly charred, avoiding an intense red heat, cool, digest with about 20 ml. of hot water, and add strong hydrochloric acid, drop by drop, until the reaction is distinctly acid. Filter into a 100 ml. volumetric flask and wash with a little hot water; the volume of the filtrate should not exceed 50 to 60 ml. Return the filter containing any unburned carbon to the platinum dish, make alkaline by wetting thoroughly with lime water, dry on a steam bath, and ignite to a white ash. Dissolve the ash in a few ml. of dilute hydrochloric acid (1:3) and add to the liquid in the 100 ml. flask, rinsing the dish with a few ml. of water. To the combined solutions add about 0.5g. of calcium chloride and a few drops of phenolphthalein indicator, then 10 per cent sodium hydroxide solution until a permanent light pink color is produced and finally dilute to mark with lime water. Mix, and filter through a dry filter. To 50 ml. of the filtrate add

0.1 *N* sulfuric acid until the pink color disappears, then add methyl orange indicator, and continue the addition of acid until the yellow color changes to pink. Boil for about one minute to expel carbon dioxide. Cool, and carefully add 0.5 *N* sodium hydroxide until the liquid assumes a yellow tinge, avoiding an excess of alkali. All the boric acid is now in the free state with no uncombined sulfuric acid present. Add about 10 g. of neutral mannitol (a volume of neutral glycerol equal to the volume of the solution may be substituted for the mannitol) and a few drops of phenolphthalein indicator. Note the burette reading and again titrate the solution with standard sodium hydroxide until a pink color develops. Add a little more mannitol (or glycerol) and if the pink color disappears continue the addition of alkali until a pink color appears again. Repeat the alternate additions of mannitol and alkali until a permanent point is reached. One ml. of 0.5 *N* sodium hydroxide solution is equivalent to 0.0309 g. of boric acid.

3.5 Fat. Place on a watch glass a pad of fat-free absorbent cotton big enough to absorb the egg sample without allowing any of it to soak through. Weigh about 10 g. of egg in a weighing bottle, pour the sample on to the cotton and obtain the sample weight by reweighing the bottle. Dry the egg on the cotton at 100°C. Trim away and discard as much as possible of the cotton that is not impregnated with egg. Cut the remaining cotton and egg into pieces with clean shears, working on a large glazed paper and taking care that none of the sample is lost. Place all the material in an extraction thimble, plug the thimble with a wad of cotton and extract with chloroform in a Soxhlet apparatus for at least 8 hours. Filter the chloroform solution of the fat through a dry, quick-acting filter paper, and rinse out the flask and paper three times with small quantities of chloroform. Receive the filtered chloroform in a weighed glass flask. Distill off most of the chloroform on a water bath, allow the last traces to evaporate in the air, then heat the residue for exactly 30 minutes at not over 105°C. in an oven. Cool in an individual desiccator for 15 minutes and weigh. Repeat until the loss in weight on heating 30 minutes is not more than 5 mg.

3.6 Examination of Fat. Saponify the fat obtained in each duplicate determinations as described above, using the procedure described under determination of unsaponifiable matter in oil. (Method No. 47) Combine the two soap solutions in one separatory funnel. Determine unsaponifiable matter, unoxidized fatty acids and oxidized fatty acids exactly as described for oil in the H series. Determine iodine value and melting point of the unoxidized fatty acids and of the unsaponifiable matter if an appreciable quantity of the latter is obtained, exactly as described in the H series.

3.7 Albumin. Using a 2 g. sample of egg proceed as directed under total nitrogen Method B5.

4. RESULTS

4.1 The water should be calculated as follows:

$$\text{Per Cent Water} = \frac{\text{g. loss in weight x 100}}{\text{g. sample weight}}$$

4.2 The ash, sodium carbonate, iron and aluminum, and calcium should be calculated as follows:

$$\text{Per Cent Ash} = \frac{\text{g. ash x 100}}{\text{g. sample weight}}$$

$$\text{Per Cent Alkalinity as } Na_2CO_3 = \frac{\text{Ml. 0.1 } N \text{ NaOH x 0.53}}{\text{g. sample weight}}$$

$$\text{Per Cent } Na_2CO_3 = \text{Per Cent Alkalinity as } Na_2CO_3 - (\text{Per Cent CaO x 1.9}) - (\text{Per Cent } Na_2B_4O_7 \text{ x 0.52}).$$

$$\text{Per Cent } (Fe_2O_3 + Al_2O_3) = \frac{\text{g. } F_2O_3 + Al_2O_3 \text{ x 100}}{\text{g. sample weight}}$$

$$\text{Per Cent CaO} = \frac{\text{g. CaO x 100}}{\text{g. sample weight}}$$

4.3 The sodium chloride should be calculated as follows:

$$\text{Per Cent NaCl} = \frac{\text{ml. 0.1 } N \text{ } AgNO_3 \text{ x 0.5846}}{\text{g. sample weight}}$$

4.4 The borates should be calculated as follows:

$$\text{Per Cent } Na_2B_4O_7 = \frac{\text{Ml. 0.5 } N \text{ NaOH x 2.525 x 2}}{\text{g. sample weight}}$$

4.5 The fat should be calculated as follows:

$$\text{Per Cent Fat} = \frac{\text{g. chloroform extract x 100}}{\text{g. sample weight}}$$

4.6 Report unsaponifiable matter, unoxidized fatty acids and oxidized fatty acids as described in H series.

4.7 The albumin shall be calculated as follows:

Per Cent Albumin = Total Nitrogen (Method B5) x 6.38

LACTIC ACID (G-4)

1. SCOPE

1.1 This method is intended for the analysis of free sulfuric acid, volatile acid, free acid and acid anydride in assaying lactic acid.

2. APPARATUS AND REAGENTS

2.1 300 ml. Kjeldahl flask.
2.2 Kjeldahl bulb trap.
2.3 200 ml. vertical spiral condenser.
2.4 250 ml. graduated cylinder.
2.5 An electric hot plate capable of regulation to give the desired distillation rate.
2.6 Lactic acid.
2.7 Neutral 95 per cent ethyl alcohol.
2.8 Phenolphthalein solution.
2.9 Standardized 0.1*N* sodium hydroxide.
2.10 Standardized 0.5*N* sodium hydroxide.

3. PROCEDURE

3.1 Free Sulfuric Acid. Dissolve 50 g. of the sample in 200 ml. of neutral 95 per cent ethyl alcohol, heat to 60°C., cover, and let stand over night in a warm place. Filter and wash with alcohol. Evaporate the alcohol from the filtrate, make up the residue to 250 ml. with water, add 5 ml. of concentrated hydrochloric acid, boil, and add barium chloride solution. Determine the precipitated barium sulfate in the usual manner. Calculate per cent free sulfuric acid.

3.2 Volatile Acid. Dilute 1 g. of sample to about 50 ml. with water and titrate with 0.5 *N* sodium hydroxide using phenolphthalein as indicator. Calculate to lactic acid (1 ml. of 0.5 *N* NaOH is equivalent to 0.045 g. of lactic acid). On the basis of this determination make up a solution of the sample containing 15 g. of lactic acid per liter. Put 150 ml. of this dilution in a long-neck 300 ml. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser. The total height from the bottom of the flask to the top of the turn connecting with the condenser shall be between 20 to 24 inches. Distill over 125 ml. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 ml. of water to the residue in the flask and repeat the distillation. Titrate the distillates, either separately or collectively, with 0.1*N* sodium hydroxide, using phenolphthalein as indicator, and calculate the total number of milligrams of acetic acid (1 ml. of 0.1*N* NaOH is equivalent to 6 mg. of acetic acid).

3.3 Free Acid and Anhydride. Titrate 50 ml. of the same dilution as used for "Volatile Acid" in the cold with 0.5*N* sodium hydroxide and phenolphthalein to the first pink. Call this the "first titration." From this value subtract the number of ml. of 0.5*N* sodium hydroxide equivalent to the sum of free sulfuric acid and volatile acid present in the 50 ml. aliquot. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as percentage of free lactic acid. After completing the "first titration" add 4 ml. or 0.5*N* sodium hydroxide in excess of 5 ml. in the case of concentrated acid and let stand at 20° – 25°C. for 15 minutes. Then add 5 ml. of 0.5*N* sulfuric acid, boil and titrate back with 0.5*N* sodium hydroxide. Determine the quantity of alkali used by the anhydride and calculate it as lactic acid.

4. RESULTS

4.1 The free sulfuric acid should be reported in per cent on the original sample.

4.2 The volatile acid should be reported in per cent on the original sample. From this value for acid found in the distillates determine by means of the accompanying distillation table the actual weight of volatile acid originally in the distilling flask and calculate it as per cent volatile acid.

4.3 The lactic acid should be reported as the percentages of lactic acid equivalent to anhydride present.

DISTILLATION TABLE

(Two Distillations)

Quantity of Volatile Acid in Distilling Flask Corresponding to Quantity of Acid Found in Distillates Under Conditions Specified. (All Values Given in Milligrams)

In distillates	In Flask	In distillates	In Flask	In distillates	In Flask	In distillates	In Flask
5	0.0	22	19.2	39	38.9	56	58.6
6	1.0	23	20.4	40	40.0	57	59.8
7	2.0	24	21.5	41	41.1	58	61.1
8	3.0	25	22.7	42	42.3	59	62.3
9	4.0	26	23.9	43	43.4	60	63.5
10	5.0	27	25.0	44	44.6	61	64.7
11	6.2	28	26.2	45	45.7	62	65.9
12	7.4	29	27.3	46	46.8	63	67.2
13	8.6	30	28.5	47	48.0	64	68.4
14	9.8	31	29.7	48	49.2	65	69.6
15	11.0	32	30.8	49	50.3	66	70.8
16	12.1	33	32.0	50	51.5	67	72.0
17	13.4	34	33.1	51	52.7	68	73.3
18	14.5	35	34.3	52	53.9	69	74.5
19	15.7	36	35.4	53	55.0	70	75.7
20	16.9	37	36.6	54	56.2	71	76.9
21	18.1	38	37.7	55	57.4	72	78.1

OXALIC ACID (G-5)

1. SCOPE

1.1 This method is intended for assaying oxalic acid.

2. APPARATUS AND REAGENTS

2.1 500 ml. volumetric flask.

2.2 Casserole.

2.3 Gooch crucible.

2.4 Platinum dish.

2.5 Standardized 0.1*N* potassium permanganate.

2.6 Standardized 0.1*N* sulfuric acid.

2.7 Standardized 0.1*N* sodium hydroxide.

2.8 Methyl red solution.

3. PROCEDURE

3.1 Oxalates (as oxalic acid). Weigh accurately about 5 g. of acid, and dissolve in water, transfer to a 500 ml. volumetric flask, and make up to the mark. Pipette 20 ml. into a casserole, and determine oxalate by titration with 0.1*N* potassium permanganate.

3.2 Insoluble Matter. If the solution above is not completely clear, the solution may be filtered through a weighed Gooch crucible before making up to volume washing the insoluble matter until the washings no longer react to acid with methyl red. Dry the crucible at 100°C., cool and weigh.

3.3 Ash. Weigh accurately about 5 g. of acid into a platinum dish and ash at dull red heat. Cool and weigh. If the amount present is more than 0.1 per cent, analyze it as directed below.

3.4 Neutral Oxalates. Any neutral oxalates will appear as sodium carbonate in the ash. Treat the ash with exactly 10 ml. of 0.1*N* sulfuric acid, let stand for a few minutes, wash the solution into a beaker, and heat to boiling to expel carbon dioxide. Cool, add a few drops of methyl red indicator and titrate the excess acid with 0.1*N* sodium hydroxide. From the volume of acid consumed, calculate percentage of neutral oxalate as sodium oxalate.

3.5 Iron, Aluminum, Calcium, and Magnesium. Determine in the solution after titrating the sodium carbonate by methods described in references cited for listed chemicals.

3.6 Sulfate, Chloride. Test portions of the solution prepared for the determination of oxalate with barium chloride and with silver nitrate. If a positive test is obtained, determine the constituent found by the usual methods.

4. RESULTS

4.1 The oxalates as oxalic acid should be calculated as follows:

$$\text{Per Cent } H_2C_2O_4 = \frac{\text{ml. } 0.1N \text{ } KMnO_4 \text{ x } 22.505}{\text{g. sample weighed}}$$

4.2 The insoluble matter should be calculated as follows:

$$\text{Per Cent insoluble matter} = \frac{\text{g. insoluble matter x } 100}{\text{g. sample weighed}}$$

4.3 The ash should be calculated as follows:

$$\text{Per Cent Ash} = \frac{\text{g. ash x } 100}{\text{g. sample weighed}}$$

4.4 The neutral oxalates should be calculated as follows:

$$\text{Per Cent } Na_2C_2O_4 = \frac{\text{ml. } 0.1N \text{ } H_2SO_4 \text{ x } 0.67}{\text{g. sample weighed}}$$

TANNERY SUGARS (G-6)

1. SCOPE

1.1 This method is intended for the analysis of moisture, ash, dextrose, purity, total sugar, dextrose before inversion and pH in assaying tannery sugars.

2. SPECIMEN

2.1 Liquids, (molasses, syrup, etc.): Mix materials of this class thoroughly. If crystals of sugar are present, dissolve them either by heating gently (avoiding loss of water by evaporation) or by weighing the whole mass, then adding water, heating until completely dissolved and after cooling, reweighing.

2.2 Semi-Solids (massecuites, etc.); Weigh 50 g. of the sample into a 250 ml. volumetric flask, treat with water, fill to the mark, and mix thoroughly; or weigh 50 g. of the sample and dilute with water to 100 g. If the insoluble material remains, mix uniformly by shaking before taking aliquots or weighed portions for the various determinations.

2.3 Solids (Sugars, etc.); Grind, if necessary, and mix thoroughly to secure uniform samples. In the case of raw sugars mix thoroughly and in the shortest possible time on a glass plate with a spatula, reducing lumps when present

with a glass or porcelain rolling pin; or mix thoroughly in the shortest possible time in a porcelain mortar, using a pestle to reduce lumps when present.

3. APPARATUS AND REAGNETS

3.1 Platinum dish.

3.2 500 ml. volumetric flask.

3.3 Baume′ hydrometer.

3.4 pH meter equipped with glass electrode.

3.5 Ammonium carbonate.

3.6 Copper sulfate solution. 72.7 g. $CuSO_4 5 \cdot H_2O$ per liter.

3.7 Alkaline Tartrate. 346 g. Rochelle salts and 100 g. sodium hydroxide made up to one liter. Let stand 48 hours and filter through asbestos.

3.8 Standardized Fehling's solution. Pipette 25 ml. each of (3.6) and (3.7) into 250 ml. sugar flask (Heat on an open gas flame to boiling point); add by means of burette 24 ml. of 1 per cent C. P. anhydrous dextrose solution. (U. S. Bureau of Standards, Standard Sample No. 41 dextrose is recommended). Boil for 10 seconds and after permitting the cuprous oxide to settle, observe color of solution. If still quite blue add a few tenths more of sugar solution, again boil, settle and note color. Repeat this operation until blue color has become very faint. Then add 2 drops of a 0.3 per cent methylene blue solution. Add sugar solution drop by drop under repeated boiling. The end point is reached at the time when the blue color gives place to a bright yellow.

If reagents used in making up the Fehling's solution were all of a strictly C. P. quality, then 0.25 g. of dextrose would be equivalent to exactly 50 ml. of Fehling's solution. This serves as a basis for the computation of the per cent dextrose in liquors of unknown dextrose content.

4. PROCEDURE

4.1 Moisture. Dry 5 g. of the sample prepared as directed under (2.3) in a flat dish (platinum) in an oven at the temperature of boiling water for 16 hours, cool in a desiccator and weigh. Dry again for an hour or until the change in weight is not more than 2 milligrams. In the case of sugars of large grain, heat at 105° - 110°C. to expel the last traces of occluded water.

4.2 Ash. Heat 5-10 g. of the sample in a 50-100 ml. platinum dish at 100°C. until the water is expelled, add a few drops of pure olive oil and heat slowly over a flame until swelling ceases. Then place the dish in a muffle and heat at low redness until a white ash is obtained. Treat the residue with a little ammonium carbonate solution, reevaporate and heat again in the muffle at a very dull red heat to constant weight.

4.3 Dextrose and Purity. Weigh accurately the number of grams of sample so as to contain close to 5 g. of dextrose. Dissolve in a little hot water and

transfer completely to a 500 ml. volumetric flask. Make up to mark, temperature 20°C. Mix thoroughly, titrate against 50 ml. of Fehling's solution as under "Standardized Fehling's solution.

(a) The quantity of methylene blue should be not more than 2 drops for glucose, 3 drops for corn sugar and 4 drops for Hydrol. The additional quantity for the latter two serves to mask the yellow color of the liquors at the last state of reduction.

(b) From the moment the indicator is dropped in, the flask should never be shaken or rotated outside the flame, otherwise the dye will reoxidize.

(c) After the indicator is in, a couple of drops of sugar solution should always be added before boiling again.

(d) The flask should under no circumstances be put down on the table between boiling after the indicator is added, because this causes cooling and consequent oxidation by the entrance of air.

(e) The entire titration period should not be greater than 3 minutes.

(f) The C. P. dextrose is dried for 1 hour at 100°C., when 20 inch vacuum is used, for standardizing Fehling's solution.

The gravimetric method for reducing sugars can be used, especially where samples are only tested occasionally.

4.4 Total Sugar. Dissolve 5 g. of sample in one liter of distilled water. Pipette 200 ml. into a 500 ml. flask and proceed as for sugars in leather as described under "Glucose", Method B10.

4.5 Dextrose before Inversion. Same as above for total sugar omitting the hydrolysis with HCl and refluxing.

4.6 pH. Make up a 22° Baume′ solution of the sample and determine pH with the glass electrode.

4.7 Foam, Scum and Melting Point. In a 100 ml. graduated cylinder place cubes of about ¼ inch size until cylinder is full. Place tube in a suitable boiling water bath. Note time to completely melt the sugar and the amount of foam and scum by volume.

5. RESULTS

5.1 The moisture content of the specimen shall be calculated as follows:

$$\text{Moisture, per cent} = \frac{W_1 - W_2}{W_1} \times 100$$

where: W_1 is the weight of the original specimen, grams.
W_2 is the weight of the dried specimen, grams.

5.2 The ash in the specimen shall be calculated as follows:

$$\text{Ash, per cent} = \frac{W_1}{W_2} \times 100$$

where W_1 is the weight of the ash, grams.
W_2 is the weight of the specimen, grams.

5.3 The dextrose and purity of the specimen shall be calculated as follows:

$$\text{Dextrose, per cent} = \frac{\text{g. dextrose equivalent to 50 ml. Fehling's sol x 100}}{\text{ml. unknown x g. sample in 1 ml.}}$$

$$\text{Purity, per cent (\% dextrose on moisture free basis)} = \frac{\text{\% dextrose x 100}}{\text{\% dry substance}}$$

5.4 The total sugar shall be calculated using the tables in B10. Calculate per centage of total sugar as follows: glucose equivalent x 600 = per cent sugar.

5.5 The pH value shall be reported to the second decimal place.

Specific Heats of Collagen and Leather

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Abstract

Determinations of the specific heats of collagen, vegetable-tanned leather, chrome-retanned leather, chrome leather, and these materials containing varying percentages of moisture were made at 25°C. The same determinations were also made on dry chestnut and quebracho tanning extracts and on a stuffing grease and an animal oil. The results obtained with the collagen and leather containing various percentages of moisture show abrupt breaks in the curves which indicate phase changes. These changes are explained on the basis of changes in the vibrational activity of the polar groups in the collagen molecule.

Lubricating materials added to leather increase the specific heat. This affects the comfort of the leather adversely during cold weather.

1. Introduction

In connection with the heats of wetting of collagen and leather [1], interest arose with regard to the specific heats of these materials. For highly ac-

curate calorimetric measurements, a knowledge of the specific heats of all components is necessary.

Although specific heat is a fundamental physical property, little information with regard to its values for leather or collagen is available in the literature. An examination of the literature located only one study of the specific heat of leather. A. Cheshire and N. L. Holmes [2] give a value of 0.263 cal/gram for dry leather and 0.321 for leather containing 16.28 per cent of water. The Handbook of Chemistry and Physics [3] gives a value of 0.36 cal/gram/degree C for the specific heat of dry leather.

An important study related to leather was made by Hampton and Mennie [4]. They determined the specific heats of gelatin gels over a temperature range of 25 °C to -180 °C. in an effort to obtain some information on bound water. They found that the specific heats of water and dry gel were not additive, and their studies yielded no reliable information on the percentage of so-called bound water in these materials.

Specific heat is an important factor in determining the comfort of wearing materials. Although not as important as the rate of conduction of heat, the amount of heat required to maintain temperature equilibrium will depend upon the heat capacity of the materials worn. This is especially noticeable in cold weather when shoes are changed.

A study of the property of specific heat is most important in the elucidation of some of the fundamental properties of a material. A determination of the specific heat of leather containing varying amounts of moisture may yield information with regard to the manner in which the two components combine. The comparison of the specific heat of collagen with that of leather may yield similar information with regard to the tanning agent and collagen.

In the present study, the specific heats of collagen and three different tannages of leather were determined at 25 °C. Determinations of specific heats were made on the dry material and on the materials containing various percentages of water ranging from 0 to 17 per cent. Specific heats were also determined for two types of tanning agents and for oils and greases used to lubricate leather.

2. Apparatus and Procedure

The calorimeter used in this work was the same as the one used in a study of the heats of wetting of collagen and leather [1]. This calorimeter was developed originally by Newman and Wells [5] to study the heats of hydration of cements.

An attempt was made in the initial experiments to make the determinations by suspending the materials in carbon tetrachloride. Carbon tetrachloride was used as the suspending liquid and heat transfer medium because it has a low specific heat (approximately 0.2 cal/g/degree C) and because it

is a nonpolar liquid which should not react with leather or collagen. A liquid of low specific heat was desired so that the accuracy of the measurement would be improved by having a greater percentage of the total heat absorbed by the sample under test.

However, the determination of specific heats by suspending the specimens directly in the liquid medium used for thermal transmission was found to be unsatisfactory. The apparent specific heats obtained in this way were quite variable and sometimes negative, which is impossible. The medium apparently reacted with the materials to take up energy or a slow solution process occurred.

In order to obtain reliable data, it was necessary to place the test specimens in a container where no direct contact was made with the heat conducting medium. The specimens were placed in small copper tubes 11 cm. in length and 1 cm. in diameter. About 2.5 g. of sample was contained by each tube. A series of ten tubes was used for a determination on each sample making a total specimen size of about 25 g. The ten tubes were wired together to form a raft and then submerged in the heat conducting medium of carbon tetrachloride. This procedure proved to be very satisfactory. The small diameter of the tubes and the intimate contact with all the tubes by the medium gave rapid thermal equilibrium.

Determinations were made at 25°C. on each sample at various concentrations of moisture. The copper tubes were filled with the leathers or collagen conditioned at 50 per cent relative humidity and 73°F. After the specific heat was determined on each specimen, the caps on the tubes were removed, the tubes and contents were placed in a desiccator, and part of the moisture was removed by means of a vacuum pump. After pumping for several hours, the tubes were removed from the desiccator, the caps were replaced, the tubes and contents were weighed, and the specific heat was determined. This procedure was continued until there was no further loss in weight on evacuation. Six to eight determinations on each specimen with varying amounts of moisture were made in this way. The specimen was finally completely dried by heating in an oven at 100°C. for 24 hours and a specific heat determination made.

Determinations in the calorimeter were made in pairs. The runs were started slightly below 25°C. After thermal equilibrium was reached, heat was added by passing a measured current from a battery through a coil having a known resistance. The temperature rise in a definite time was determined and when thermal equilibrium was again reached, the procedure was repeated. This gave two determinations of the heat capacity of the system for each run, one slightly below 25°C., the other slightly above 25°C. If the two determinations did not check within 0.5 per cent, the run was repeated. The average of the two determinations was used to calculate the specific heat.

The average deviation from the mean of a single determination of specific heat was about 3 per cent. This is equivalent to a standard deviation of ±0.01 in the specific heat.

3. RESULTS

The results of determinations of specific heats of collagen, chrome-retanned leather, vegetable-tanned leather, and chrome-tanned leather are given in table I. These results include measurements made on the materials containing varying percentages of moisture and also determinations on the materials dried by heating for 24 hours at 100°C. Chemical analyses of the collagen and leathers are given in table II.

TABLE I

Specific Heats of Collagen and Leather Samples at 25° C.

Collagen		Chrome-retanned leather		Vegetable-tanned leather		Chrome-tanned leather	
Moisture content	Specific heat	Moisture content	Specific heat	Moisture content	Specific heat	Moisture content	Specific heat
%	cal/g/deg C	%	cal/g/deg C	%	cal/g/deg C	%	cal/g/deg C
0	0.3723	0	0.3404	0	0.3334	0	0.3045
1.02	0.3490	1.52	0.3287	1.15	0.3202	1.98	0.2918
1.96	0.3659	2.12	0.3266	1.32	0.3274	3.69	0.3631
4.56	0.4014	4.23	0.3448	2.59	0.3280	7.59	0.3576
6.49	0.4061	7.23	0.3458	3.85	0.3844	9.39	0.3737
17.03	0.4280	9.23	0.3474	6.20	0.3730	11.07	0.3893
		11.29	0.3606	7.83	0.3835	13.46	0.3841
				9.31	0.3844	14.96	0.4098
				10.81	0.4129		

TABLE II

Chemical Analysis of the Leathers (Moisture- and Grease-Free Bases)

	Hide substance	Ash	Cr_2O_3	Vegetable tannin by difference
	%	%	%	%
Collagen	100.7	——	——	——
Vegetable-tanned leather	52.06	0.24	——	47.70
Chrome-retanned leather	59.87	2.20	1.80	34.82*
Chrome-tanned leather	88.85	——	4.25	——

*Calculated by using the conversion factor 2.73 to convert Cr_2O_3 to the basic chromium sulfate tanning agent and the value for the difference between percentage ash and percentage Cr_2O_3 [12].

In order to obtain some information on the specfic heats of materials used in leather making, determinations were made on chestnut and quebracho

tanning extracts. These materials were dried at 100°C. for 24 hours before the determinations were made. Measurements were also made of the specific heats of stuffing grease and of animal oil (neat's foot). The stuffing grease was obtained by extracting it from a sample of chrome-retanned upper leather. The values obtained for the specific heats of the tanning materials and the lubricating materials are given in table III.

TABLE III

Specific Heats of Leathermaking Materials at 25°C.

Material	Specific heat
	cal/g/deg C
Chestnut tannin extract (powder) dry	0.2889
Quebracho tannin extract (solid) dry	0.3152
Stuffing mixture (extracted from upper leather)	0.5162
Animal oil	0.5191

4. Discussion

The variation of the specific heat with moisture content for collagen, chrome-retanned leather, vegetable-tanned leather, and chrome-tanned leather is shown in figure 1. As the moisture content of the sample increases from 0 to 1 or 2 per cent, the specific heat passes through a minimum. This behavior occurs with all of the samples. After the minimum, there is a sharp increase in the specific heat as the moisture content increases. After the sharp rise, the curves reach a plateau where the specific heat is nearly constant until the moisture content reaches about 9 per cent. Beyond this point, the specific heat increases further with increase in moisture content. The plateau region occurs for each of the three leathers. For collagen, the number of determinations in this area was insufficient to establish the exact shape of the curve.

Breaks in the curves showing the increase in a physical property with moisture content are not unexpected. However, studies on moisture adsorption [6], heats of wetting [1], and dielectric constants [7, 8] have failed to reveal any abrupt changes with increase in moisture content. The sorption of moisture by a protein is undoubtedly similar to the formation of hydrates in inorganic compounds. The sorption of moisture over a wide range of relative humidities would be expected to form a series of hydrates. This series of hydrates should correspond to different compounds having different properties. From studies of the moisture relations of leather and other proteins by the above-mentioned procedures, it has been found that the energy of combination of moisture decreases as the amount of moisture is increased. The rate of decrease has, however, in all instances been characterized by a smooth curve indicating that the precision of the measurements was not great enough to detect a discontinuity which would be characteristic of a change in phase.

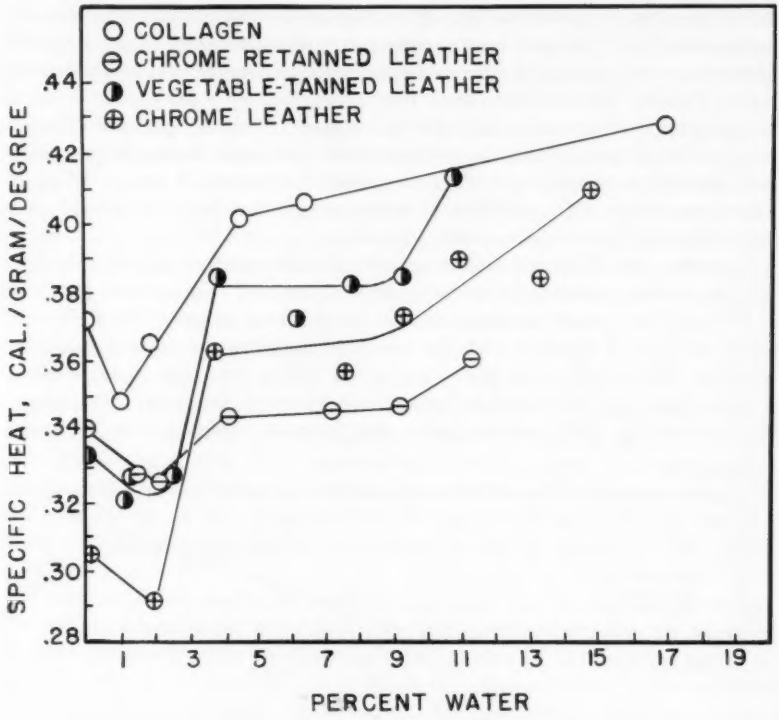

FIGURE 1.—Variation of the Specific Heat with the Percentage of Water in the Materials.

Studies of the heat of wetting [1] show that the greatest amount of heat is evolved in the adsorption of the initial amounts of water by the dry materials. The adsorption of this amount of moisture apparently lowers the activity of some of the atoms, decreasing the magnitude of their vibrations so that they absorb less energy. This would produce a minimum in the specific heat. The addition of moisture beyond about 2 per cent apparently forms additional vibrational sites, for an abrupt increase in the specific heat occurs.

It has been suggested [9] that the first water molecules adsorbed by a protein are taken up between two polar groups. This would definitely lower the activity of the two groups and might correspond to the minimum for specific heat at about 2 per cent moisture adsorption. In further addition of moisture it was assumed that each group would adsorb a molecule of water. The abrupt rise in specific heat would then correspond to the point where the bridge between atoms formed by one molecule of water was broken and the vibra-

tional freedom of the atoms was again increased. The plateau region in the curve from 3 to 9 per cent may correspond to the adsorption of one molecule of water per polar group in the protein molecule to complete a mono-molecular layer. Pauling [9] gives data to show that approximately 9 per cent of water is required for a mono-molecular layer in collagen. Beyond 9 per cent of moisture, the polar groups may be saturated with one water molecule per group and possibly a second layer with two molecules per polar group is begun. This corresponds to the addition of more energy-absorbing vibrational sites and the specific heat shows a further increase.

Hampton and Mennie [4] determined the specific heats of gelatin gels containing varying percentages of water at temperatures ranging from 25°C. to -180°C. Their mean results over the temperature range of 0°-25°C. are shown in figure 2 together with the results obtained in the present study for collagen. The specific heat of dry collagen is higher than that of dry gelatin. When collagen is hydrolyzed to form gelatin by heating in water, a shrinkage reaction occurs with rearrangement and internal compensation of active

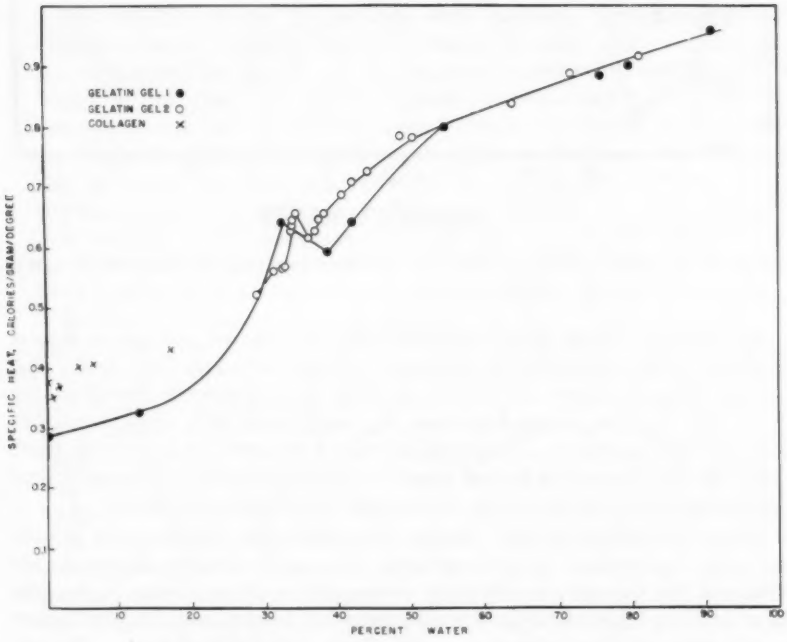

FIGURE 2.—Variation of the Specific Heats of Collagen and of Gelatin with the Percentage of water in the Samples.
Data for gelatin from Hampton and Mennie.

polar groups. It is, therefore, expected that gelatin would have a more inactive structure with fewer free polar groups to absorb vibrational energy than collagen. For this reason the specific heat of collagen would be expected to be higher.

The results on gels by Hampton and Mennie as shown in the curve in figure 2 show a break which indicates a phase change at a moisture content of approximately 32 per cent. There are not sufficient determinations with the gels at low concentrations to indicate whether there are any discontinuations in the curve at exactly the same points where they occur with collagen and leather. The gel-water system also does not exactly parallel the collagen or leather-water system. The former system borders on solution, whereas the latter represents a system of a solid and a vapor at low concentration.

Many attempts have been made in studies of protein-moisture systems to derive conclusions in regard to the amounts and properties of the so-called bound and unbound water present. This is sometimes done by subtracting the calculated value for a physical property based on that for the dry material from the total value for the constant when water is present, with the assumption that the difference can be attributed entirely to the water content. By the application of this procedure to the results obtained for the specific heats of collagen and leather in this study, the values shown in table 4 were obtained.

These calculated results obviously have no significance except to show that the specific heats of the dry leather and the water present are not additive to give the specific heat of the conditional material. A negative apparent specific heat is obtained for water when the concentration in the collagen or leather is low. At higher concentrations the apparent specific heat of water is positive but varies with the type of leather. The actual specific heat of water at 25 °C. is 0.998 cals/g/degree C.

Determinations of bound and unbound water in a protein-water system are questionable. The so-called protein-water system is probably a hydrate which behaves as a compound differing in properties from that of either the dry protein or the pure water. As the percentage of water increases, the properties of the compound change; the activity of the water increases but it re-remains restricted in mobility as would be expected in multilayer formation. The fact that water is adsorbed by a material is sufficient basis to conclude that its mobility has been restricted. There is apparently no sharp boundary line between bound and unbound water.

Specific heats of the dry leathers are lower than that of dry collagen. In table III values for the specific heat of chestnut and quebracho extracts are given. The specific heat of vegetable-tanned leather is approximately midway between that of the vegetable extracts and collagen. As shown in table II, the percentage of tannin in vegetable-tanned leather is approximately 50 per cent. It, therefore, appears that the influence of the tannin on the specific

TABLE IV

Calculation of Apparent Specific Heat of Water at 25°C. in Leather Assuming that Specific Heat of Leather is same as for Dry Material

No.	Material (Conditioned)	Material (dry)	Water	Heat absorbed by dry material	Specific heat	Heat absorbed by conditioned material	Heat absorbed by water	Apparent Specific heat of water
	g	g	g	cal/deg C	cal/g/deg C	cal/deg C	cal/deg C	cal/g/deg C
				COLLAGEN				
1	27.6561	23.6313	4.0248	8.7979	0.3723	11.8368	3.0389	0.7550
2	25.1661	23.6313	1.5348	8.7979	0.3723	10.2199	1.4220	0.9265
3	24.7080	23.6313	1.0767	8.7979	0.3723	9.9178	1.1199	1.0401
4	24.0947	23.6313	0.4634	8.7979	0.3723	8.8163	0.0184	0.0397
5	23.8733	23.6313	0.2420	8.7979	0.3723	8.3318	−0.4661	−1.9260
6	23.6313	23.6313	0	8.7979	0.3723	8.7979	0	0
				CHROME-RETANNED LEATHER				
1	25.7699	23.1547	2.6152	7.8819	0.3404	9.2926	1.4107	0.5394
2	25.2911	23.1547	2.1364	7.8819	0.3404	8.7861	0.9042	0.4232
3	24.8295	23.1547	1.6748	7.8819	0.3404	8.5860	0.7041	0.4204
4	24.1352	23.1547	0.9805	7.8819	0.3404	8.3218	0.4399	0.4486
5	23.6451	23.1547	0.4904	7.8819	0.3404	7.7215	−0.1604	−0.3271
6	23.5058	23.1547	0.3511	7.8819	0.3404	7.7264	−0.1555	−0.4429
7	23.1547	23.1547	0	7.8819	0.3404	7.8819	0	0
				VEGETABLE-TANNED LEATHER				
1	26.9572	24.3265	2.6307	8.1103	0.3334	11.1302	3.0199	1.1479
2	26.5916	24.3265	2.2651	8.1103	0.3334	10.2212	2.1109	0.9319
3	26.2307	24.3265	1.9042	8.1103	0.3334	10.0596	1.9493	1.0237
4	25.8336	24.3265	1.5071	8.1103	0.3334	9.6354	1.5251	1.0119
5	25.2632	24.3265	0.9367	8.1103	0.3334	9.7112	1.6009	1.7091
6	24.8566	24.3265	0.6301	8.1103	0.3334	8.1861	0.0758	0.1203
7	24.6467	24.3265	0.3202	8.1103	0.3334	8.0699	−0.0404	−0.1262
8	24.6065	24.3265	0.2800	8.1103	0.3334	7.8780	−0.2323	−0.8296
9	24.3265	24.3265	0	8.1103	0.3334	8.1103	0	0
				CHROME-TANNED LEATHER				
1	27.5517	23.9660	3.5857	7.2973	0.3045	11.2918	3.9945	1.1140
2	27.1922	23.9660	3.2262	7.2973	0.3045	10.4434	3.1461	0.9752
3	26.6188	23.9660	2.6528	7.2973	0.3045	10.3626	3.0653	1.1555
4	26.2176	23.9660	2.2516	7.2973	0.3045	9.7970	2.4997	1.1102
5	25.7848	23.9660	1.8188	7.2973	0.3045	9.2213	1.9240	1.0578
6	24.8509	23.9660	0.8849	7.2973	0.3045	9.0244	1.7271	1.9517
7	24.4395	23.9660	0.4735	7.2973	0.3045	7.1306	−0.1667	−0.3521
8	23.9660	23.9660	0	7.2973	0.3045	7.2973	0	0

heat of the leather is additive. Chrome leather has a lower specific heat than that of the other leathers. The Handbook of Chemistry and Physics[3] gives a value of 0.200 cal/g/degree as the specific heat of $Cr_2(SO_4)_25H_2O$. There is,

however, not sufficient chromium sulfate in chrome leather to reduce the specific heat to the value found if the values are assumed to be additive. It is probable that the chromium sulfate reduces the vibrational activity by forming cross links in the collagen molecule. The formation of cross links is in accordance with the most widely accepted theory of chrome tanning [10].

The comparatively high specific heats of the lubricating materials (Table III) used in leather diminish the comfort of the leather in cold weather by accelerating the removal of heat from the body. Greases and oils are not firmly adsorbed by the leather. They adhere to the leather by filling the pores and form an intimate mixture. It is, therefore, expected that the specific heats of leather and the lubricating materials would be additive and the combination of the two would have a higher specific heat than that of leather alone. It has also been shown that both moisture and grease increase the heat conductivity of the leather [11]. The combination of these factors would, therefore, further diminish the comfort of the leather containing lubricating materials.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Edwin S. Newman for permission to use the calorimetric equipment and for his interest in the work, and to R. R. Stromberg, T. J. Carter, and C. E. Weir for assistance in operating the equipment.

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Received, June 24, 1955

The Effect of Leather and Tannages on Photographic Plate

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Abstract

For the first time, the effect of the leathers and tannages on photographic plate has been observed. It has been shown that leathers treated with certain tanning materials which are oxidizable and reducible become photographically active. From these experiments, for the first time, the mechanism of the action is correlated to the presence of oxidizable and reducible substances in the materials that exhibit the effect, like paper, wood, leather etc. The phenomenon is shown to be of interest to the leather chemist and the potentialities of further studies are pointed out. The probable mechanism of the effect has also been discussed.

It has been known that substances like wood are endowed with the property of acting on a photographic plate in the dark and imprinting on it an image The phenomenon is known as the Russell Effect[1]. This property has been ascribed to the action of hydrogen peroxide, released from the material under test, reacting with the photographic plate either when it is in contact with or slightly separated from the plate. The action is found to persist even when a filter paper is inserted between the plate and the material. An extensive study of this phenomenon has been undertaken by one of us and the results have been reported[2]. They indicated that, apart from wood, rosin, tannin and the like produced a similar effect on the photographic plate.

A casual remark was made as early as 1898[3] that materials other than wood, such as paper, leather, etc., will also produce a similar effect on a photographic plate. Except for this remark, there is no work reported in the literature about this phenomenon with respect to leathers. So, a thorough study was considered desirable. It was thought that such a study might throw further light, not only on the mechanism of this photographic activity, but also on some difficult problems in leather chemistry. For this purpose, leathers specially prepared by different tannages and also commercial leathers have been exposed and the results are recorded in this paper.

Experimental:

A. *Preparation of the pelt*: Pieces cut from the butt portions of cow and buffalo hides and goat and sheep skins were soaked, limed, unhaired and delimed according to the customary procedure. The pelt so obtained was de-

hydrated in changes of alcohol and acetone and the resultant materials kept as stock samples.

B. *Tanning*: Portions of this dehydrated pelt were then treated with different tanning materials as below:

a. *Mineral tannages*: 33% basic chrome sulfate.
33% basic aluminum chloride.
33% basic aluminum sulfate.

b. *Vegetable tannages*: Wattle extract; Divi-divi.

c. Benzoquinone.

d. Formaldehyde.

e. Fish oil.

f. Sulfochlorinated mineral oil (Imergan).

g. Salicylic acid syntan.

h. *Combination tannages*: Chrome-aluminum.
Chrome-vegetable (Semi-chrome, chrome retan and chrome-vegetable tannage in a single bath.)

i. Vegetable tanned retanned with (1) cationic, (2) anionic and (3) nonionic chrome salt.

j. Vegetable tanned leather treated with (1) basic and (2) acidic dyes.

The pelt was tanned under standard conditions and the excess material removed by washing with water and air-dried in the shade.

C. *Commercial leathers tested were*: (1) E. I. Kip, (2) E. I. buffalo, (3) E. I. goat, (4) E. I. sheep, (5) sole leather, (6) glace kid, (7) box sides, (8) chamois, (9) semi-chrome, (10) retan leather and (11) willow calf.

D. *Photographic procedure*: The leathers were placed on the sensitized surface of a photographic plate in absolute darkness and secured in position with rubber bands. The plate was thereafter put in a card-board box and the box itslelf was placed in a specially designed light-proof box. Every care was thus taken to exclude the possibility of any stray light leaking in and vitiating the results. The arrangement was allowed to stand in the dark room for 48 hours.

The plates were then taken out and processed in the usual way under exactly identical conditions. This is very necessary as the density of the image depends not only on the time of exposure but also on the time and temperature of development and the nature of the developer used. The plates were developed for 5 min. at 75°F. using I.D2[4] developer and rinsed

in cold water for 7 min. They were thereafter fixed using G-303 fixing bath for 10 min.

The plates used for the above experiments were the Zenith Super Sensitive plates manufactured by M/s. Ilford Ltd., London. This is a non color sensitised plate of medium speed, medium contrast and medium grain. It had a speed of 24° – Day Light (B. S. I) and a range of spectral sensitivity (2300 – 5200 Å).

Data and Discussion:

1. *Effect of pelt*: The collagenous material (dehydrated pelt), as such, does not affect the photographic plate and the thickness or the source of the material (cow, buffalo, sheep and goat) also has no effect.

2. *Effect of tannages*: The leathers tanned with mineral tanning agents such as chrome and aluminum either alone or in blends do not act on the plate. Similarly, no effect was observed with formaldehyde tanned leather, oil-stuffed lace leather, Imergan tanned and syntan tanned leathers. On the other hand, the dehydrated pelt which does not affect the photographic plate, when tanned with fish oil (Figure I), vegetable tannins like wattle

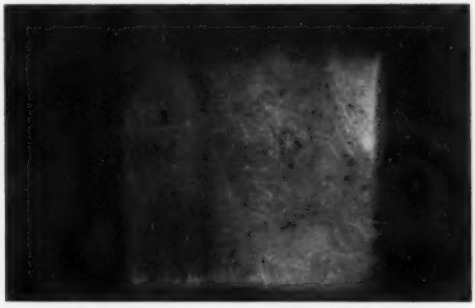
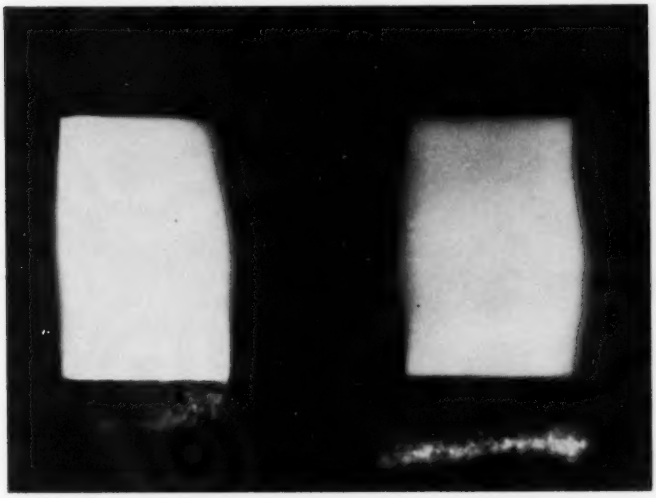


FIGURE I—Fish oil tanned leather.

extract (Figure II), divi-divi (Figure III), quinone (Figure IV), acts on the photographic plate, giving a dense picture, which may be seen from the plates. Similarly, the leathers tanned with chrome and aluminum which do not act on the photographic plate, when retanned with vegetable tanning materials, give the effect. Commercial leathers (vegetable tanned) such as E. I. kip, buffalo, goat and sheep skins, chamois leathers and chrome retan leathers gave dense pictures whereas chrome tanned leathers such as glace kid, willow calf, box sides did not.

It is very clear, therefore, that certain tanning agents do have an effect and certain others do not on the photographic plate. It is known that vegetable

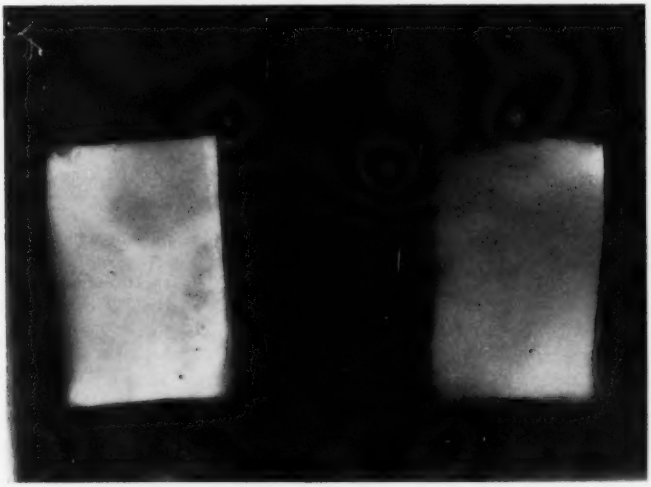


Leather tanned with Wattle Extract

Thick buffalo hide

Thin cow hide

FIGURE II—The action exerted through the black paper used as marks is also noticeable in the picture.

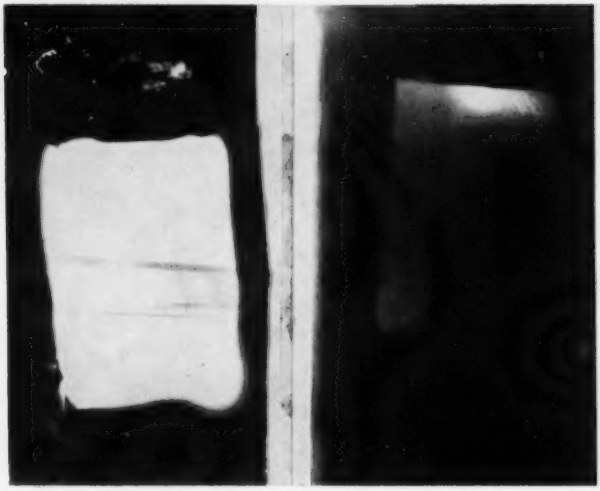


Divi-Divi tanned leather

Thick buffalo hide

Thin cow hide

FIGURE III



Thick buffalo hide Thin cow hide

FIGURE IV—(Notice the difference in activity between the thick and thin hides.)

FIGURE V—Tannin Blocks.

tanning materials and fish oils are readily oxidizable and reducible and it is quite likely that, to obtain the effect on the photographic plate, a material that is readily oxidizable and reducible must be present in the leather.

To further confirm this idea, a block of wattle extract and a block of rosin have been exposed in the dark on the photographic plate. It is seen from Figures V and VI that rosin and tannins give dense pictures even in the dark.

FIGURE VI—Rosin Block

3. *Effect of charge*: When a material is kept in contact with the photographic plate, the charge on the plate as well as the material may have an important role to play. To clarify this point, pelt, treated with cationic, anionic and nonionic chrome solutions, was obtained and kept in contact with the photographic plate in total darkness. No picture was given. Leathers tanned with syntans (salicylic acid base), formaldehyde and sulfochlorinated oils acted similarly. On the other hand, vegetable tanned leathers, when retanned with cationic, anionic and nonionic chrome solutions, gave pictures; similarly, the leathers pretreated with the above chrome solutions, when retanned with vegetable tanning materials, affect the photographic plate. The charge has apparently no influence on this effect.

4. *Density of the pictures*: From the experimental results, it has been observed that the density of the pictures given by the leathers on photographic plate is related to the thickness of the leather and the amount and nature of the oxidizable and reducible material present in it. Leathers tanned with quinone, for instance, give a much denser picture as compared to those tanned with fish oil and vegetable tanning materials. The density of the picture may, however, be increased or reduced by suitable additions or subtractions of the reactive material or by activating or inactivating it. From Figure VII, it is seen that the density of the image of the vegetable tanned leather is increased when it it further treated with an acid dye, and decreased when the same is treated with a basic dye. The same effect has been observed by treating the photographic plate with suitable dyes to increase or decrease the sensitivity of the plate.

The activity may be increased by exposing the leather to sunlight. Figure VIII indicates that this phenomenon is invigorated when a vegetable tanned leather is exposed to sunlight.

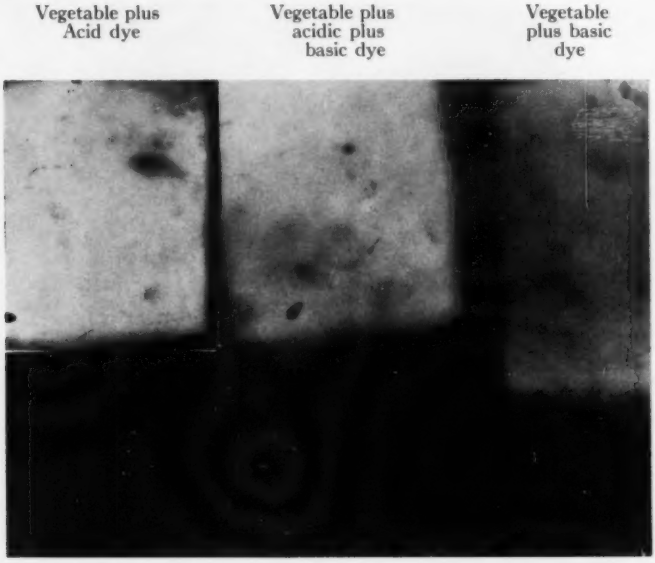


FIGURE VII—No action is observed in the case of leather covered with silver leaf and also plastic.

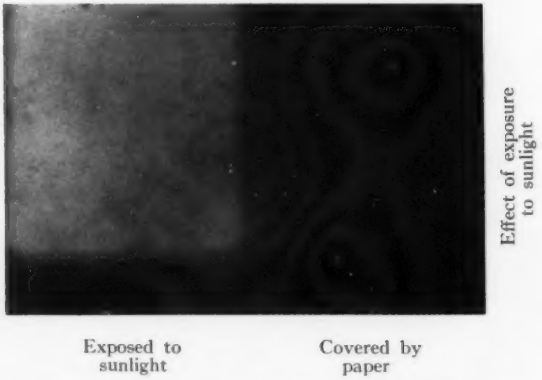


FIGURE VIII—(Notice the increased activity in the exposed regions.)

5. *Porosity*: Russel contended that wood or similar materials affect the photographic plate by releasing hydrogen peroxide. Some experiments in this connection are of interest. The vegetable tanned leathers which affect the photographic plate in the dark, still give a picture even when kept at a distance without any contact with the plate and even when a filter paper is inserted between the plate and the material (Figure IX). When the same

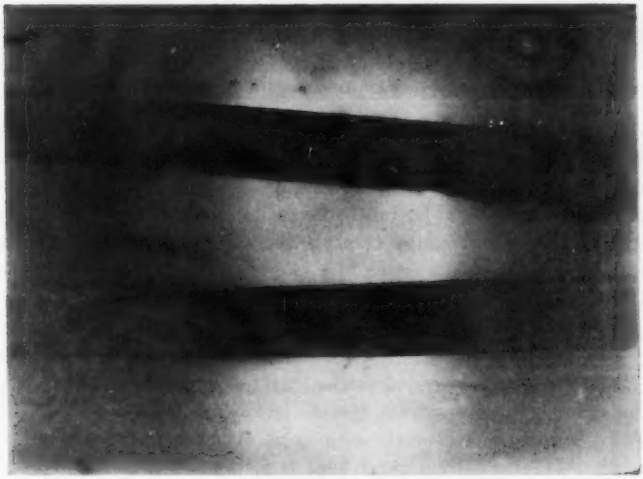


Plate showing the action when the leather and the plate are not in contact.

FIGURE IX—The leather was supported on two glass plates about 2 mm. thick and exposed to the plate. Though less sharp and defined, it still gives a picture

material is completely covered with a silver leaf, blocking the porosity of the leather, the action is arrested. These results indicate very clearly that the material under test must be porous and the air is likely to catalyse the reaction. As a further confirmation, a plastic material which has no porosity has been found to give no picture. It is to be noted, however, that these experiments do not indicate that this phenomenon is due to the hydrogen peroxide released. They only show that air and porosity have a positive part to play in this reaction. Therefore, Russel's 'peroxide theory' awaits confirmation by more conclusive researches.

6. *Radio activity*: This phenomenon is stopped by the interposition of a sheet of thin mica or cellophane or silver leaf and is also absent in panchromatic emulsions. It is well known that β and γ rays in any radio active emission pass through thin sheets of mica and cellophane and through silver leaf and also affect all types of plates including the panchromatic. It is, therefore, clear that this phenomenon is not a case of radio activity. It would be difficult to visualize the property of radio activity in leathers.

Some of the above observations are of immense interest to the leather chemist. For example, if one has to distinguish between a chamois leather tanned by fish oil and the one tanned with Imergan, quite a good deal of laborious chemical analysis is necessary and even then the results are not conclusive. A simple exposure of these pieces on the photographic plate for 24 or 48 hrs. will readily show whether the leather was tanned with fish oil or Imergan. Similar advantages may be found with regard to the other tannages and to explain the mechanism of various tannages. This technique may prove a valuable tool in the hands of the leather chemist in understanding the complex mechanism of the various treatments given to leather.

7. *Mechanism*: Russel postulated that this phenomenon is due to the action of H_2O_2 released from the material under test reacting with photographic plate. This may be the case where such peroxides are liberated. But it is not essential that it should be only hydrogen peroxide. It could be any organic or inorganic peroxide. The air may catalyse the material present, to release such peroxides but this is only a conjecture and no definite proof is available for it.

The effect seems to be capable of other explanation than by the 'peroxide theory'. It may be explained alternatively on the following lines. The reducing or oxidizing substance present in the material under test are catalysed by the air containing oxygen, carbon dioxide and water, releasing therefrom radicals such as OH, O_2^- etc., and these, in turn, may react with the reactive groups of the photographic plate, though kept at a distance, thereby producing the fogging on the plate. Such a free radical mechanism may happen even when the porous filter paper is kept in between. But such an action is not possible if the material is covered with a non-porous medium. It is to be remembered that this again is a postulate and no evidence is put forward in this paper to substantiate it. Work is in progress in the direction of a correct appraisal of the mechanism of this effect.

At this point, one thing appears certain. Any material that shows this phenomenon (other than radio active material) should contain an oxidizable and reducible substance.

Conclusions:

Treating the pelt (collagenous material) with different tanning agents, it has been shown that:

1. The collagenous material does not affect the photographic plate in darkness.

2. The collagenous material when treated with tanning agents which are oxidizable and reducible such as vegetable tannins, benzoquinone and fish oil gives intense pictures on the photographic plates in darkness; but leathers

tanned with materials like chrome, aluminum, formaldehyde, syntan and sulfochlorinated mineral oils do not show this effect.

3. The effect may be increased or decreased by the amount and the nature of the tanning material and by deactivating or further activating by sunlight or other suitable materials.

4. The charge on the tanning material or on the leather has no effect on this phenomenon.

5. Porosity is considered essential for the material under test.
and

6. The presence of a reducible or oxidizable material is considered essential for giving this phenomenon.

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Received April 27, 1955.

A Study of the Effect of Tryptic Enzyme on Collagen

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Abstract

Collagen that has been in contact with bating enzymes shows an excessive tendency to dissolve in hot water. Evidence is here presented that bating enzymes are adsorbed on collagen and are the cause of this effect. This evidence comes from: (1) direct determination of the adsorption by measurement of the loss of enzymatic activity of the bating solution and by measurement of the enzymatic activity of the treated collagen, (2) a study of the rate at which hot water dissolves treated collagen, and (3) a study of the effect of the time of contact with the bating enzymes on the amount of collagen dissolved.

The soluble products formed from collagen were characterized by analytical and paper chromatographic methods.

*Ernest Griess Fellow.

Introduction

In view of the interest in the action of trypsin on skin and hide during bating, it was decided to investigate more fully a recently discovered phenomenon which might throw more light on this process. It has long been known that only negligible amounts of water-soluble products are formed when collagen is treated with trypsin at 34°C. However, Thaureaux [17] has shown that, if such a pre-treated collagen is subsequently heated in water at 70°C., it dissolves much more rapidly than does untreated collagen under the same conditions.

This effect has been attributed to changes induced by the enzyme at 34°C. in making collagen less resistant to hot water, presumably involving the weakening of intermicellar and intermolecular forces, or "prepeptization" [3, 4]. Another explanation of this effect that has been advanced [7] is that it is due to trypsin which was adsorbed on the collagen at 34°C. and which acts on the denatured collagen at 70°C. before it is inactivated.

The purpose of this study was to investigate this effect more completely from a number of different points of view; the new evidence might then be found to favor one or the other of the alternative explanations.

Experimental

1. *Reagents and Analytical Procedures.*

The "collagen squares" used in these experiments were approximately 1 inch squares of unlimed, solvent-dehydrated, steerhide corium collagen. The "ground collagen" was this same collagen preparation ground in a Wiley mill to pass a 4 mesh screen. The trypsin was U.S.P. grade; the buffer was Sorensen's phosphate buffer (0.1M, pH 7.6).

Total nitrogen was determined by the modified Dahl-Oehler Kjeldahl method [13]. Tryptic activity was measured by the Kunitz casein digestion method [9]. In this method a buffered casein solution is incubated with trypsin; the extent of digestion of the casein by the trypsin is determined by precipitating the protein from the mixture with trichloroacetic acid and measuring the optical density of the supernatant with a spectrophotometer in the ultraviolet region (280 mμ). The Neuman-Logan [6] colorimetric method was used to analyze for hydroxyproline, a characteristic amino acid of collagen, and the Stein-Moore ninhydrin method [16] for amino nitrogen. The latter method was used to give an approximate measure of the number of amino groups liberated when collagen dissolves in hot water. Paper chromatography, using the ninhydrin reagent to detect the presence of amino acids and peptides, was carried out essentially according to the procedures of Rockland, Blatt, and Dunn [14].

2. *Measurement of Tryptic Activity of Trypsin Solution After Incubation With Collagen.*

If the Thaureaux Effect is caused by the action of trypsin which has been adsorbed by collagen, it might be possible to show this loss of tryptic activity in a trypsin solution in which collagen has been incubated at 34°C.

Ten ml. buffer, 4 mg. trypsin, and 100 mg. ground collagen were incubated together for 1 hour at 34°C. In the control, the collagen was omitted from the mixture. The solutions were then filtered and the tryptic activity of each solution was determined. This experiment was replicated 4 times.

The trypsin solutions which had been incubated with collagen showed an average of 8 per cent less tryptic activity than the trypsin solutions which had been incubated without collagen. A t test [2] showed that this difference may be significant, but is not necessarily so. It can be concluded that, if any trypsin is adsorbed on collagen, it is, under these conditions, of the order of magnitude of only 10 per cent.

3. *Measurement of Tryptic Activity of Collagen After Incubation With Trypsin Solution.*

In these experiments collagen that had been incubated at 34°C. with trypsin was tested directly for tryptic activity. One hundred mg. ground collagen, 4 mg. trypsin, and 10 ml. buffer were incubated together at 34°C. Three controls were run: (1) buffer only, (2) trypsin and buffer, and (3) collagen and buffer. Two different incubation periods were used—5 minutes and 60 minutes. At the end of the incubation period each solution was passed through filter paper. The tryptic activity of an aliquot of each solution was determined. The incubated collagen samples were well washed with water; 1 ml. of buffer was added to each collagen sample and the tryptic activities of each suspension was determined by the same method.

With the 5 minute incubation period, 9 per cent of the trypsin was adsorbed on the collagen; in each of two experiments with 60 minute incubation periods, 12 per cent of the trypsin was adsorbed. Collagen controls which had been incubated with buffer had no tryptic activity. The trypsin solution showed a loss of 8 per cent activity with the 5 minute incubation period; in the one experiment with the 60 minute incubation period in which the tryptic activity of the trypsin solution was measured, there was a 7 per cent loss of activity. The measurements of the quantities of adsorbed trypsin are also of the same order of magnitude as those obtained indirectly (measurement of loss of tryptic activity of trypsin solutions) in the experiments of Section 2. These experiments provide direct support of the adsorption theory.

4. *Measurement of Tryptic Activity at 70°C.*

If the activity of adsorbed trypsin is assumed to be the cause of the Thaureaux Effect, it must be proved that trypsin (which, like other enzymes, is heat-inactivated) does not lose its activity too rapidly at 70°C. to account for the effect. A literature search showed that the heat inactivation of trypsin is erratic; it depends on the purity of the preparation and on the conditions of inactivation [8]. A study was therefore made of the activity of this particular trypsin preparation under the conditions of the Thaureaux Effect.

Ground collagen (1 g.) was incubated at 34° C. for 1 hour in 100 ml. buffer. The collagen was filtered off, washed, and then heated 2 hours at 70°C. with 40 mg. trypsin in 100 ml. water. 73 per cent of the collagen nitrogen dissolved.

In a similar control experiment with the trypsin omitted, only 35 per cent of the collagen nitrogen dissolved at 70°C. Under these conditions, therefore, trypsin is still active at 70°C.

Two parallel experiments were run to test whether the small amount of trypsin that might be adsorbed (equivalent to approximately 10 per cent of the amount of trypsin used in the previous experiment; see Sections 2 and 3) would be sufficiently active at 70°C. to account for the effect. In the control carried out under the usual Thaureaux Effect conditions, 1 g. ground collagen was incubated at 34°C. with 40 mg. trypsin and 100 ml. buffer for 1 hour. The collagen was filtered off, washed, and then heated at 70°C. for 1 hour with 100 ml. water. 47 per cent of the collagen nitrogen dissolved. In the experimental sample, the collagen was similarly treated at 34°C. except that trypsin was not added. The washed collagen was then heated at 70°C. for 1 hour with 100 ml. water and only 4 mg. trypsin (the expected amount of adsorbed trypsin). 48 per cent of the collagen nitrogen dissolved.

Since the percentage of dissolved collagen nitrogen is approximately the same in these two experiments, it can be concluded that the amount of trypsin that might be adsorbed on the collagen would be sufficiently active at 70°C. to account for the Thaureaux Effect.

5 *Effect of Heating Time at 70°C.*

If the Thaureaux Effect is due to adsorbed trypsin, there should be a decrease in the rate at which the trypsin-treated collagen dissolves at 70°C., because the trypsin would gradually lose its activity at this temperature. In time, only the slow, non-enzymatic solubilization of collagen would occur. This type of time curve would not necessarily be expected if a "prepeptization" of collagen had occurred during the 34°C. incubation.

Ground collagen (1 g.) was incubated at 34° C. with 40 mg. trypsin and 100 ml. buffer for 1 hour. The collagen was then well washed with water and heated at 70°C. with 100 ml. water for 10 minutes. Similar experiments were run with incubation times at 70°C. of 20 minutes, 40 minutes, 60 minutes, and 120 minutes. The averages of milligrams of collagen nitrogen dissolved per minute during these time intervals in two such series of experiments are given in Table 1. The results show that the reaction proceeds rapidly during the initial phase, but that even after the first 10 minutes the rate falls off steeply.

TABLE I

Effect of Heating Time at 70°C. on the Amount of Collagen Dissolved in Thaureaux Effect

Time Interval	Average Mg. Collagen N Dissolved Per Minute During Interval	
	Exp. 1	Exp. 2
0–10 min.	2.99	3.79
10–20 min.	1.28	0.83
20–40 min.	0.31	0.90
40–60 min.	0.52	0.18
60–120 min.	0.13	——

To determine whether the rate of inactivation of trypsin at 70°C. parallels the decrease in rate of the reaction in the previous experiment, a series of experiments were run which were identical with the preceding series except that the trypsin (4 mg.) was added only at the beginning of the 70°C. incubation. The results are given in Table II. They show that trypsin which

TABLE II

Effect of Heating Time at 70°C. on Amount of Collagen Dissolved With Trypsin Added at 70°C.

Time Interval	Average Mg. Collagen N Dissolved Per Minute During Interval
0–10 min.	2.36
10–20 min.	1.98
20–40 min.	0.84
40–60 min.	0.60

has been added at 70°C. gives the same general type of time curve as that obtained in the Thaureaux Effect. This similarity in inactivation behavior provides further support for the adsorption theory.

6. *Effect of Incubation Time at 34°C.*

Adsorption is a fast process; equilibrium is reached between the adsorbent and the solution in a short time. Consequently, if adsorbed trypsin is assumed

to be the cause of the Thaureaux Effect, the amount of collagen dissolved at 70°C. in a given time would be expected to be practically independent of the time of incubation of the collagen with trypsin at 34°C. On the other hand, if the trypsin is exerting a chemical "prepeptizing" action on collagen, then the amount of "prepeptization" of collagen (and therefore the amount later dissolved at 70°C.) would be expected to increase with an increase in the length of the 34° C. incubation.

The effect of the time of the incubation period at 34°C. on the amount of collagen dissolved at 70°C. was therefore studied. Two hundred mg. ground collagen was incubated at 34°C. with 8 mg. trypsin and 20 ml. buffer. Three such experiments were run with different periods of incubations: 10 minutes, 60 minutes, and 120 minutes. The filtrates from the mixtures were analyzed for nitrogen. The collagen samples were washed well with water and then heated in 20 ml. water at 70°C. for 60 minutes. The filtrates were analyzed for total nitrogen. The results are given in Table III. They show

TABLE III

Effect of Incubation Time at 34°C. on Amount of Collagen Dissolved

Time of Incubation at 34° C.	% Original Collagen Dissolved at 34° C.	% Original Collagen Dissolved at 70° C.
10 min.	0.0%	38%
60 min.	0.0%	39%
120 min.	0.6%	36%

that the process which occurs at 34°C. in the presence of trypsin is a fast one, since the per cent of original collagen nitrogen dissolved at 70°C. is independent of the time of incubation at 34°C. These results, therefore, support the adsorption theory.

The results of Section 3, in which the amount of trypsin adsorbed on collagen was measured, also indicated that adsorption is essentially complete after only 5 minutes at 34°C.

7. Inactivation of Trypsin.

If adsorbed trypsin is the cause of the Thaureaux Effect, then treatment of collagen which has adsorbed trypsin with a reagent which inactivates the trypsin should prevent the Thaureaux Effect. The reagent itself should, of course, not react with the collagen. Since there is an appreciable non-enzymatic reaction, it is necessary that the trypsin inactivation be practically complete in order to detect with assurance the effect of inactivation.

A search has therefore been made for such an inactivator, but without success. Inorganic substances which are general enzyme inhibitors, such as

fluoride, cyanide, or sulfide, do not inhibit trypsin[15]. Basic formaldehyd- inactivates trypsin[10], [12], as also do many protein reagents[11], but these cannot be used because they also react with collagen. Alkali which is sufficiently strong (0.1*N*) to inactive trypsin reacts with collagen; organic solvents, such as acetone, ethyl alcohol, and methyl alcohol, which do not affect collagen, do not inactivate trypsin. A study of the effect of a trypsin inhibitor on the Thaureaux Effect therefore could not be undertaken.

8. *Study of the Thaureaux Effect with Collagen Squares.*

A study was made of the effect of incubation with trypsin on the hot water solubilization of collagen squares. A 1 inch collagen square (1 g.) was incubated at 34° C. for 1 hour with 40 mg. trypsin and 100 ml. buffer. The collagen was well washed with water and then incubated at 70°C. for 1 hour with 100 ml. water. A control experiment was run with the trypsin omitted. 2.7 per cent of the original collagen nitrogen of the trypsin-treated sample dissolved at 70°C.; 1.8 per cent of the collagen nitrogen of the control sample dissolved. Since this resistance to attack might possibly have been due to the fact that the squares (which had been kept in the dry state for some months) were only slowly wetted during the 34°C. incubation, the previous experiment was repeated with collagen squares which had been soaked in buffer overnight in the refrigerator. With these squares 2.2 per cent of the original collagen nitrogen of the trypsin-treated sample dissolved at 70°C.; 1.8 per cent of the collagen nitrogen of the control sample dissolved. Non-wetting was, therefore, not an important factor in preventing the solution of the squares. Both trypsin-treated and control squares were much more resistant to solution than those of Gustavson[4]; these differences are probably due to different methods of preparation of the squares and to the different conditions used in studying the Thaureaux Effect.

Liming of the collagen squares before the reaction would be expected to make the squares more susceptible to attack by trypsin, as some degradation of collagen might occur in liming[4]. Two squares were given mild liming by soaking in a saturated lime solution for 24 hours at 5°C.; they were delimed with dilute hydrochloric acid and then soaked overnight in buffer before the Thaureaux Effect experiment was carried out. With these limed squares, 1.8 per cent of the original collagen nitrogen of the trypsin-treated sample dissolved at 70°C.; 1.3 per cent of the collagen nitrogen of the control sample dissolved.

These results with the limed collagen squares are not in disagreement with previous demonstrations of a positive Thaureaux Effect with limed collagen squares. In one series of experiments, neutral calfskin pelt was cut into small (3 x 3 x 1 mm.) squares before bating[4]; in the second, the 1 inch calfskin squares used were obtained in the limed state from a tannery and were there-

fore undoubtedly subjected to more severe liming conditions than the present squares[3]. In both cases, the bating conditions differed from those used in the present study. When these differences are taken into account, the results of the present experiments are seen to be not in direct contradiction to those previously obtained.

The resistance of the collagen squares to attack by trypsin is not unexpected for two reasons: (1) the surface available for adsorption of trypsin is not so great as that of the ground collagen, and (2) even light mechanical treatment of collagen, such as cutting into small cubes, is known to make it more susceptible to tryptic action[1].

If trypsin is adsorbed on the collagen squares but does not act on it at 70°C. because trypsin cannot attack native (unground) collagen, it might be possible to show the presence of the adsorbed trypsin by grinding the square before the hot water treatment. The following experiment was carried out to test this point. Four collagen squares (two trypsin-treated and two control squares) were incubated at 34°C. exactly as the squares in the first experiment of this section. All the squares were then well washed, dehydrated with acetone, air-dried, and ground in a micro-Wiley mill to pass a twenty mesh screen. Each preparation was then heated with water (1 ml. per 10 mg. collagen) for 1 hour at 70°C. 2.2 per cent and 2.1 per cent of the original collagen nitrogen of the trypsin-treated squares dissolved; 1.9 per cent and 1.8 per cent of the collagen nitrogen of the control squares dissolved.

Since the squares were treated subsequent to the trypsin incubation in a way which should not have inactivated the trypsin, these results seem to indicate that there was no adsorption of trypsin on the collagen squares. However, the collagen of the control squares was also resistant to solution, even though it was ground to pass a finer mesh than the usual "ground collagen". If the reasonable assumption is made that the acetone does not affect the collagen, then these experiments suggest that important changes occur in ground collagen during the 34°C. incubation period (even in buffer only) which cannot occur with native (unground) collagen. This effect of grinding can be explained by assuming that, although it reduces the collagen to particles of a large size relative to molecular dimensions, some changes must occur which are of importance in enzyme attack, such as opening up of the fibrils. In support of this idea that grinding produces profound changes in collagen is the evidence of Highberger and Kersten[5] that prolonged grinding in the Wiley mill changes its X-ray diffraction pattern.

9. *Study of the Products Formed in the Thaureaux Effect.*

With a mixture of peptides, it is common practice to estimate roughly the average number of amino acid residues constituting the peptide chains as the ratio of total nitrogen to amino nitrogen. This ratio gives only the order

of magnitude of the peptide length, as it does not take into account such sources of error as the presence of amino acids containing more than one nitrogen atom and the difficulties of determining the amino nitrogen content of a complex mixture.

The results from such analyses on the filtrates from the hot water (70°C.) treatment of ground collagen indicate that the order of magnitude of the size of the average peptide is the same, whether the products were formed in the Thaureaux Effect, in the non-enzymatic reaction, or in the reaction in which trypsin is added at 70°C. If the molecular weight of the average amino acid residue of the peptides is assumed to be 100, then the average molecular weight of the peptides formed in this reaction is of the order of magnitude of 5,000. However, it should be noted that these conclusions were drawn from the ratio of two numbers, one large and the other small, and that small errors in the measurement of the smaller number necessarily result in large errors in the ratio.

The ratio of the total nitrogen of collagen to the hydroxyproline nitrogen is a fixed value. If collagen is partially solubilized and the ratio of total nitrogen to hydroxyproline nitrogen is determined on the soluble portion, then the value of this ratio that is obtained might be the same or different than the value for collagen. It will be the same if the collagen is dissolving as fragments of approximately the same hydroxyproline content as the protein; it will be different if small peptides which contain either less or more hydroxyproline than the protein form the solubilized portion. By a determination of this ratio, then, it might be possible to gain some insight into the type of reaction which occurs when collagen dissolves.

This ratio was determined on the filtrates formed from the three types of reaction studied (the Thaureaux Effect, the non-enzymatic reaction, and the reaction in which trypsin is added at 70°C.). Since the Neuman-Logan method determines free hydroxyproline, it was necessary to hydrolyze the samples by boiling for 16 hours with 6*N* hydrochloric acid before the hydroxyproline analyses. Within the relatively large experimental error of the method, the ratios of total nitrogen to hydroxyproline nitrogen were identical with that of collagen. From these data there is no evidence, therefore, that peptides of different hydroxyproline content than the protein are formed when collagen is solubilized by hot water.

In order to determine whether any amino acids or small peptides were present in the filtrates from both the 34°C. and the 70°C. incubations from the three types of reactions, the filtrates were examined by paper chromatographic methods. Two solvent mixtures were used: *n* - butanol-acetic acid-water (4:1:5) and pyridine-water (80:20). After the papers were chromatographed, they were developed with ninhydrin. A similar paper chromatograph was made of the trypsin which had been used, since it might

be expected to contain some impurities which could be detected by this very sensitive method. As the trypsin preparation was still present in some of the filtrates of the 34°C. incubations, it was important to eliminate, as possible products of the reaction, ninhydrin-positive substances coming from the trypsin preparation.

After the contributions from the impurities in the trypsin were taken into account in those instances where it was necessary, no ninhydrin-positive substances which could be attributed to amino acids or small peptides were found in the products. In all the three different types of reaction, then, there is no evidence that, when collagen dissolves, small fragments of the protein are formed.

Summary

A study has been made of the Thaureaux Effect. The tryptic activity of trypsin solution after incubation with ground collagen shows a possible decrease of approximately 10 per cent; the collagen shows a corresponding amount of tryptic activity. These results supply the most direct evidence for the assumption that the Thaureaux Effect is caused by adsorbed trypsin.

Further indirect evidence in support of this theory comes from two other facts: (1) the rate at which the enzyme-treated collagen dissolves at 70°C. decreases rapidly, and parallels the rate obtained when trypsin is added at 70°C., and (2) the amount of collagen dissolved at 70°C. is independent of the time of the 34°C. incubation.

The Thaureaux Effect could not be demonstrated with collagen squares, either limed or unlimed. A study of the products of the reaction indicated that no small peptides or amino acids are formed when collagen dissolves under the conditions of these experiments.

Acknowledgment

Appreciation is expressed to the staff of Tanners' Council Laboratory for suggesting this problem and for advice and counsel during the course of this work.

Received February 17, 1955.

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Received February 22, 1955.

ABSTRACTS

The Effect of the Floor on Foot Temperature. By R. W. Muncey and J. M. Hutson. *Australian Journal of Applied Science*, **4,** No. 3, 395 (1953). Floors of concrete are commonly unacceptable because they are claimed to make the feet cold. The temperature of the feet when shod, however, depends largely on the environment. A physiological hypothesis to connect these factors quantitatively is proposed and from it calculations of the effect of the floor on the foot temperature are made. A confirmatory experiment is described and it is deduced that a person's feet will be warmer on concrete than on other floors in about 40 per cent of randomized cases. Floors of high thermal inertia and low temperature may tend to increase the coldness of feet already cold, but it is fallacious to attempt a remedy by attention to the floor; an increased environmental temperature is necessary. R.B.K.

Pressures on the Human Foot During Walking. By T. S. Holden and R. W. Muncey. *Australian Journal of Applied Science*, **4,** No. 3, 405 (1953). Instantaneous pressures developed on the sole of the foot during walking in ordinary shoes on any floors can be measured with the following described equipment. To measure the pressure on the sole of the foot from the sole of the shoe, a sensitive element is required which will fit readily into any shoe without affecting the wearer's gait. The pressure-sensitive element, essentially a double condenser, was built up of alternate sheets of tin foil and pimple rubber, cemented together with a rubber solution, and cured by applying heat and light pressure. Overall, the gauge was about 1/8-inch thick, was the shape of part of the insole of a shoe, and had a sensitive area of about 1/2 sq. inch. The capacity of the gauge was made part of the circuit of an oscillator which was strapped to the subject's leg clear of the calf muscle. Capacity changes due to pressure on the sensitive area of the gauge gave frequency modulated signals which were fed through a cable to a discriminator and thence deflected a cathode ray tube which was photographed. Auxiliary equipment, which included one electronic metronome to print an indexing mark on the film every 0.33 seconds and another to give an audible signal to guide the subject's walking rate, was mounted with the amplify-

ing and recording apparatus on a trolley. The connecting cable was held so that it would not interfere with the subject's gait. Large variations in the shape of the pressure-time curve occur from one person to another, but the step to-step variations of any one person are very much less. Variation in the rate of walking changes the ordinates and abscissae approximately in inverse proportion. Variations due to changes in floor surface are almost non-existent, the only noticeable effect being the disappearence of a small impact peak when the subject changes from ordinary floors (concrete, wood) to lawn. R.B.K.

How Skin and Hide Defects Affect Leather. By F. O'Flaherty. *Leather and Shoes,* **129,** No. 20, 51 (1955). Two groups of defects interest every tanner: those which occur before the skin or hide arrives at the tannery, and those which happen in the course of processing. On the farm or range the animals are subject to injury and disease, the latter including those parasitic conditions which are so costly to the tanner. The author lists some of the more common injuries such as: Wire and brier scratches, nail damage, bruise damage which is the cause of great losses in meat as well as in the skin, prod damage from both nails, forks and electric prods and also chain damage. Diseases which affect the animal skins, and pertinent information on each are given. Diseases listed are: Erysipelas, allergy rashes, tuberculosis of skin, parasitic damage such as lice and ticks, manges such as scabies and follicular mange, the larder beetle, fungus infection, grubs which cause estimated millions of dollars damage each year. In the case of grubs or warble fly, experiments, using organic compounds for dosing the cattle, have been successful in killing the grub larvae and thus breaking the life cycle. Hyperkeratosis or X-disease is a condition which has been reported only during the past two decades. Found first in only one state, within a few years was found in practically every state as well as in foreign countries. In 1952 it was discovered that the disease was due to the animals swallowing grease which contained chlorinated napthalene. During 1954 the reduction of defects in leather from this disease has been observed, and is due to the avoidance of oils or greases containing chlorinated napthalene. Defects caused in the tannery include damage in the cure due to poor storage facilities, oversoaking, mistakes in adding sulfide, excessively high bate temperatures, stick and kiss marks in the wet process, molding in the blue or during drying and machine damage. R.B.K.

The Practice Of Hide Curing. By R. M. Lollar and F. O'Flaherty. *The Leather Manufacturer,* **72,** No. 2, 8 (1955). The process of curing is a process of dehydration of the hide, replacing some of the lost water by curing salt and concentrating the protein concentration of the hides to some extent. This is illustrated by the data given in Table No. I. Four red-haired, seventy pound native steer hides were taken immediately after flaying and rapidly sampled in eight areas over each side. After sampling, one side of each hide was salted with a mixture of coarse and fine salt; the other side was brined in saturated brine for twenty four hours. Both halves were rolled hair side out and placed in a covered crock in the refrigerator at 40° F. each side remaining in cure for 30 days before the sampling for cured hide analysis, taking the samples adjacent to the eight sampling locations used before curing. The figures given are the average for these eight area analysis in each case. The protein content of these hides was fractionated by the method described by Jacobs [*J.A.L.C.A.* **44,** 722 (1949)]. Table II shows the data secured on the four skins whose composition is shown in Table I. The practical tanner has long recognized three indications of poor cure which are evident upon inspection of the hides. They are, first, strong ammoniacal, fishy or offensive odor, secondly, hair slippage and third red heat. Microscopic examination of thin sections cut from hides suspected of poor cure can supply additional evidence. Approximately 300 hides from eleven different commercial lots of hides have been examined and analyzed. Data are given in Table III. The following characteristics of

TABLE I

The Composition of Native Steer Hides

Component of Hide	Hide No.	Fresh Hides Side for Salting	Fresh Hides Side for Brining	Cured Hides Salted Side	Cured Hides Brined Side
	1	62.3	63.0	43.4	48.6
Water—%	2	64.5	63.0	44.7	47.8
(Benzene Distillate)	3	61.1	63.5	45.5	50.4
	4	62.4	61.7	43.9	47.1
Salt—% Ash	1	0.55	0.66	15.1	10.8
(Residue after 16 hours	2	0.82	0.94	15.2	10.4
at 600°C.)	3	0.80	0.78	14.9	10.9
	4	0.78	0.84	14.0	10.2
	1	31.0	31.4	35.2	34.7
Protein—%	2	32.0	32.5	34.5	35.0
(% Kjeldahl Nitrogen x 5.62)	3	32.6	32.7	37.4	35.7
	4	33.3	32.7	39.8	37.5
	1	6.05	4.94	6.3	5.9
Grease, Etc.—%	2	2.68	3.56	5.6	6.8
(By Difference)	3	5.50	3.02	2.2	3.0
	4	3.52	4.76	2.3	5.2

TABLE II

The Protein Fractionation of Native Steer Hides

Nitrogen Fraction as % of Total Nitrogen	Hide No.	Fresh Hides Side for Salting	Fresh Hides Side for Brining	Cured Hides Salted Side	Cured Hides Brined Side
Non-Protein Nitrogen-%	1	1.0	1.1	1.8	1.5
(Not precipitated by	2	1.7	1.6	1.6	1.5
trichloracetic acid)	3	1.5	1.5	1.6	1.7
	4	1.5	1.6	1.6	1.6
Elastin-Kevatin Nitrogen-%	1	4.9	4.1	6.3	5.8
(Grain area proteins	2	5.4	4.9	6.2	6.2
not solubilized by HLC)	3	6.2	5.9	7.2	7.3
	4	5.9	6.2	5.3	6.2
Globular-Protein Nitrogen-%	1	5.5	5.7	5.1	4.5
(Protein nitrogen precipitated	2	6.8	7.3	5.0	4.6
by 3.7% trichloracetic acid	3	6.9	6.8	4.5	4.7
and 4.8% salt)	4	7.5	7.0	4.9	4.5
Collagen Nitrogen	1	88.6	89.1	86.8	88.2
(Protein nitrogen precipitated	2	86.1	86.2	87.6	87.3
only by 30% trichloracetic	3	85.4	85.8	86.7	86.3
acid)	4	85.1	85.2	87.3	88.6

well cured hides seem to be required based upon the data presented. (a) Quality of curing workmanship, a maximum postmortem time of two hours for take off. The total tare loss to the tanner should be held to 20 per cent of the cured to hide weight. The curing salt used should be new, and of proper crystal size for prompt solution without caking. Curing and storage temperatures should be kept low, preferably below 70° F. and near to 32° F.

TABLE III
Characteristics of Commercial Cured Hide Lots
First 10 Lots Salt Cured; Last Lot Brine Cured

Hide Lot Source	Lot Evaluation Number Hides Sampled	Tare Per Cent	Cure Evaluation	Composition of Tared Hides As received basis Water Per Cent	Salt Ash Per Cent	Protein Per Cent	Coll-agen Per Cent of Protein	Grease Per Cent	Cure Index Vol. N / Tot. N %
H 439 Country-Locker	40	15.1	Fair	45.3	14.9	37.3	91.7	2.7	0.20
H 440 Small Packer Locker	40	19.5	Dried	42.9	17.6	37.2	90.4	3.0	0.23
E 749 Heavy Steer D.C. Salt	40	23.0	O.K.	44.3	14.4	37.3	84.9	4.5	0.27
R 282 Mississippi Small Packer	12	19.0	O.K.	46.2	13.7	38.0	84.2	2.1	0.29
R 319 Small Packer Car	8	17.9	O.K.	43.1	15.3	38.5	85.2	2.4	0.30
R 320 Indianapolis Packer	10	18.0	O.K.	43.9	14.8	38.4	84.1	2.9	0.31
R 318 Missouri Small Packer	15	18.1	O.K.	43.4	15.2	37.4	84.9	3.5	0.32
ASH Suspected Greasy Lot	20	26.9	Fair	43.1	14.2	38.7	88.4	3.2	0.34
CAL California Packer	50	27.7	Poor	40.8	14.7	40.2	81.2	3.3	0.56
LAN Kansas City Packer	20	24.4	Poor	36.2	19.5	41.1	73.8	2.4	0.96
BPS Brined-Packer	40	32.7	O.K.	48.0	13.0	36.5	87.5	1.6	0.23

(b) Cured hide moisture content. Cured hides prepared by salting should contain 40-45 per cent water; brined hides may contain up to 50 per cent water. (c) Cured hide salt content. The salt content should not be less than one third the water content in well cured salted hides. (d) Hide volatile nitrogen content. The hides should preferably contain .20 to .30 per cent volatile nitrogen on the total nitrogen basis. (e) Hide leather making content. The hide should contain at least one quarter of its weight as hide collagen, when examined as the hide lots in this report. R.B.K.

The Fastness of Dyestuffs on Leather. By F. P. Russel and T. C. Mullen. *J. Soc. Leather Trades' Chemists*, **39**, 70 (1955). There has been a tendency to turn to other

TABLE I.
Light Fastnesses of Tannages.

No.	Tannage and after-treatment	Light Fastness
1.	Full chrome, neutralised and dried	4—5
2.	Full chrome, crusted with 1% non-ionic wetting agent	4—5
3.	Full chrome, fatliquored with 2% Turkey Red Oil	4
4.	Full chrome, fatliquored with 2% Sulphated Neatsfoot	4
5.	Full chrome, fatliquored with 2% Sulphated Cod Oil	4—5
6.	Rechromed alum, neutralised and dried	4—5
7.	Alum tanned	4—5
8.	Quebracho	1
9.	Chestnut	3
10.	Myrabolams	3
11.	Mimosa	1
12.	Full chrome, sumach mordant	4—5
13.	Full chrome, myrabs mordant	4
14.	Full chrome, gambier mordant	4—5
15.	Full chrome, light-fast syntan mordant	4—5
16.	Full chrome, normal syntan mordant	4
17.	Aldehyde tannage	3—4

materials when color fastness is important. Hence the leather trade has need to focus its attention on fastness and consider steps for improvement. Examples of leathers requiring fastness to light are suede shoe, gloving, clothing and bookbinding leathers. Apart from clothing and gloving leathers washing fastness is not normally needed. Shoe linings and hat band leathers must also include fastness to perspiration. Dyes in common use, even in the same classification, are not characterized by uniform fastness properties. Therefore it is necessary to possess knowledge of the individual members of the same class. Dyes which produce exceptional fastness on textiles may not act similarly on leather. This means that failure to remain fast may be due more to the properties of the leather than to the quality of the dye. Hence a range of tannages on sheepskin skivers was assessed for light fastness by the standard method against the Society of Dyers and Colorists light fastness standards. In this test standards and samples are exposed to north daylight until a change is discernible in the sample. Comparison with the standards enables an assessment to be made on the light fastness scale of 1-8. The light fastness for the 17 tannages is given in Table I.

It is plain that, as a class, vegetable tannages are less fast than chrome. Four dyes were selected with varying fastness to light and washing, and the 17 tannages dyed with them.

TABLE II.

Fastness of Dyestuffs Employed

Dyestuff	Light	Washing
A. Napthalene Leather Yellow R200 (C.I.274)	6	4
B. Napthalene Leather Brown 2RS	4	3
C. Coomassie Navy Blue G200 (C.I.289)	3	2
D. Napthalene Leather Green GS (C.I.666)	1	1

TABLE III.

Effect of Tannage on Light Fastness of Dyestuffs

No.	Tannage	Undyed	Dyestuffs A	B	C	D
1.	Full chrome, neutralised and dried	4–5	<5	3	2	1
2.	Full chrome with 1% non-ionic agent	4–5				
3.	Full chrome with 2% T.R.O.	4		Omitted		
4.	Full chrome with 2% S.N.O.	4				
5.	Full chrome with 2% S.C.O.	4–5				
6.	Rechromed alum	4–5	<5	3–4	2	1
7.	Alum	4–5		Omitted		
8.	Quebracho	1	1	1	1	1
9.	Chestnut	3*	4	4	3	2
10.	Myrabolams	3*	4–5	4	3	2
11.	Mimosa	1	1	2	1	1
12.	Sumach mordant	4–5	<5	3–4	2	2
13.	Myrabs mordant	4	<5	3	2	2
14.	Gambier mordant	4–5	<5	4	2	1
15.	Light fast syntan mordant	4–5	<5	3	2	2
16.	Normal syntan mordant	4	4–5	2	1	1
17.	Aldehyde	3–4		Omitted		

*The dulling effect of exposure on these tannages appears to compensate partly for the fading of the dyestuff and gives apparent fastness. This is also the explanation of apparent improvement in some cases with dyestuff D.

Table II gives the data relative to the dyes and Table III gives the results obtained with the dyed leathers with respect to light fastness.

For washing fastness the samples, to which had been attached a piece of wool cotton material, were placed in a 40 to 1 liquor, containing 5 g. neutral soap flakes per liter, in an oscillatory dyeing machine at 40° C. After drying, the change in the dyed pattern and the extent of staining on wool and cotton were assessed. Table IV gives the results on the tannages selected for the test, with the effect assessed by reference to the International Grey Scale The effect of basic dyestuff was also examined. The four dyestuffs described above were dyed on gloving leather and topped with a range of four common basic dyestuffs. The results of washing tests on these leathers are given in Table V.

TABLE V.

Effect of Basic Dyestuffs on Washing Fastness

Dyestuff	Washing Fastness: Without agent				Agent before				Agent after			
	D	U	W	C	D	U	W	C	D	U	W	C
A Naphthalene Leather Yellow R 200	3–4	4	4	3	1	3	3	2	3	2	3	3
B Naphthalene Leather Brown 2RS	2	4–5	4–5	3	1	3	4	3	2	2	4	3
C Coomassie Navy Blue G 200	1	3	4	2	1	2	3	1	2	2	3–4	2
D Naphthalene Leather Green GS					1	3	3–4	4	1	3	4	3–4
— Basic dyestuff alone on mordant chrome leather					1	3	3	3	1	2	3	3
A Naphthalene Leather Yellow R 200					3–4	2	3	3	3	3–4	4	3
B Naphthalene Leather Brown 2RS					2	2	3–4	2	2	3	4	3
C Coomassie Navy Blue G 200					1	2	3	2	1	3	3–4	2
D Naphthalene Leather Green GS	1	3	4	4–5	1	3	3	3	1	2	3	3–4
— Basic dyestuff alone on mordant chrome leather					1	2	3–4	3	1	3	4	3

* These headings refer as follows:—

D—dyed leather.
U—Staining of undyed leather
W—staining of wool
C—staining of cotton

TABLE IV.

Effect of Tannage on Washing Fastness of Dyestuffs

Dyestuff	Washing Fastness: Without agent				Agent before				Agent after			
	D	U	W	C	D	U	W	C	D	U	W	C
1. Full chrome	4–5	4–5	3–4	4–5	5	3–4	2	4	3	1	5	5
6. Rechromed alum	1	4	3	1	4–5	3	1	4	3	1	5	5
8. Quebracho	1	4	3	1	4	3	1	4	3	1	4	4–5
11. Mimosa	1	4	3	1	4	3	1	4	3	1	4–5	4–5
12. Sumach mordant	2	4	3	2	4	3	1	4	3	2	5	5
13. Myrabs. mordant	4	4	3	2	4	3	1	4	3	1	4–5	5
14. Gambier mordant	3–4	4	3	2	4	3	1	4	3	1	5	5
15. Light fast syntan mordant	3	4	3	2	4	3	1	4	3	1	5	5
16. Normal syntan mordant	4	4	3	2	4	3	1	4	3	2	4–5	4–5

Comparison of the fastness of topped dyeings with that of the anionic dyestuffs alone shows that, generally, the washing fastness is not reduced by the presence of basic dyestuffs. Levelling agents are usually of poor to average light fastness and their effect on dyestuffs is progressive, reducing total fastness as the amount increases. See Table VI. The effect on washing fastness is less significant. See Table VII. Checking this with both pretreatment and aftertreatment with a cationic agent showed an improvement in washing fastness for only one case. In a like manner the effect on light fastness showed no direct relation between fastness and treatment. See Table VIII and IX.

TABLE VI.

Effect of Levelling Agent on Light Fastness

1% Naphthalene Leather Brown 2RS Light Fastness	4	3–4	3	2–3

TABLE VII.

Effect of Levelling Agent on Washing Fastness

A Naphthalene Leather Yellow R200	3	4–5	3	4	3	4–5	3	4	2	4–5	3	4	2	4–5	3	4
B Naphthalene Leather Brown 2RS	2	4–5	3	4–5	2	4–5	3	4–5	2	4–5	3	4–5	2	4–5	3	4–5
C Coomassie Navy Blue G 200	1	3–4	2	4	1	3–4	3	4	1	3–4	3	4	1	3–4	3	4
D Naphthalene Leather Green GS	1	4	4–5	4–5	1	4	4–5	4–5	1	4	4–5	4–5	1	4	4–5	4–5

TABLE VIII.

Effect of Cationic Fixing Agent on Washing Fastness

Dyestuff	Without agent				Agent before				Agent after			
	D	U	W	C	D	U	W	C	D	U	W	C
Naphthalene Leather Brown ADS	1	4	4	2	1	4	4	2	1	4	4	2
Naphthalene Leather Brown GDS	1	4–5	4–5	4	2	4–5	4–5	4	1	5	4–5	4
Naphthalene Leather Brown TNS	3	4	4–5	4	3–4	4	4–5	4	3–4	4–5	4–5	4
Naphthalene Leather Brown GRS	1	4	3–4	3	1	4	3–4	3	1	4	4	3
Naphthalene Leather Violet 2RS	2	3	4	4	2	3	4	4	2	3–4	4	4
Lissamine Green BN 200	1	3–4	4	4	2	4	4	4	3–4	4	4	4–5

TABLE IX.

Effect of Cationic Fixing Agent on Light Fastness

Dyestuff	Untreated	Light Fastness Before Dyestuff	After Dyestuff
Naphthalene Leather Brown ADS	3	2	1
Naphthalene Leather Brown GDS	3	3	2
Naphthalene Leather Brown TNS	1	2	1
Naphthalene Leather Brown GRS	2	2	1
Naphthalene Leather Violet 2RS	2	2	2
Lissamine Green BN 200	1	1	1

A study of the effect of increasing amounts of formic acid for exhaustion showed no improvement from the increased acid once the pH of the bath had been lowered sufficiently to exhaust it. The diazotizing and developing process for certain direct dyes might be expected to affect the fastness. A range of these dyestuffs, with various developers, was dyed on leather. Again the results were inconclusive, some showing a decided improvement and some apparently no effect. The final conclusion is that each individual case must be decided on its own merits. The results depend both on the method of tanning and the dyestuffs employed. With the exception of light fastness, no accepted standards or methods of assessment exist. These must be clearly defined with reference to the dyed leather and not merely to the dyestuffs used. As methods of tanning are fully as important as quality of dyes, consultation and agreement between interested parties is an essential prerequisite to the establishment of standards and methods. The increasing importance of color fastness makes such cooperation between dyers and tanners of interest to both. R.H.T.

Study of the Affinity of Black Wattle Extract Constituents. Part I. Affinity of Polyphenols for Swollen Collagen and Cellulose in Water. By D. G. Roux. *J. Soc. Leather Trades' Chemists*, **39**, 80 (1955). The paper consists of a study of the affinity of tannin constituents, and some polyphenols of known structure, for collagen and cellulose as measured in chromatographic columns. The columns were prepared by pouring slurries of well soaked hide powder and cellulose into identical 1.5 cm. diameter tubes plugged with glass wool, making columns 4 inches long. The columns were washed 1 hour to remove solubles. In a preliminary study of flavanols (robinetin and quercetin), 2-8 dihydroflavonols (dihydrorobinetin and dihydroquercetiin - also called taxifolin), 3-4-dihydroxyflavanes, 3-hydroxyflavanes and the polyhydroxy phenols (pyrogallol and gallic acid), it was found that the flavanols had a high affinity for both collagen and cellulose, although much higher for cellulose. The remaining classes moved through the columns with relative ease. In further tests a mixture of about 10 mg. each of the same materials were subjected to the usual chromatographic process using water only as an irrigant. When the first trace of polyhydroxyphenol appeared ($FeCl_3$ test), development of the column was discontinued. Excess fluid at the top of the column was pipetted off and the column allowed to drain completely. The column was then extruded upon a glass plate and cut into sections which were immediately extracted with a 50-50 mixture of acetone and water. The extracts were dried under reduced pressure in a current of nitrogen at 30-40°C. and the residue spotted on two dimensional paper sheets (Whatman No. 1). The chromatograms were irrigated with butanol/ acetic acid/ water for one direction and with water only for the other. Green tea poly-

phenols, the same enzymatically oxidized by fermentation, black wattle and quebracho were also examined in this manner. The wattle was methanol extracted from fresh bark, the quebracho was natural, unsulfited. From these studies it was concluded that, with the exception of flavanols, a parallel exists between the affinity of various polyphenols for collagen and for cellulose in water. Paper chromatograms may, therefore, be used to interpret differences and changes in the affinity of the major black wattle polyphenols towards collagen. The abnormally high affinity of the flavanols for cellulose may be due to their extremely low solubility in water, their planar nature of their strongly resonating nature. The affinity of the individual polyphenols for collagen varies enormously and is dependent on a combination of various physical and chemical factors, e.g. solubility in water, spatial orientation, molecular size and the number and position of functional groups. The affinity properties are considered to operate even under the very altered conditions of practical tannage, a fact which appears to have been largely overlooked by the protagonists of the different theories of tannage. R.H.T.

The Catalytic Action of Metals on Vegetable Tanned Leather Stored In An Atmosphere Containing Sulfur Dioxide. By R. H. Hall and R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **39**, 92 (1955). It has been shown that vegetable tanned leathers deteriorate more rapidly during storage if they contan appreciable amounts of copper and iron. Ionic iron in the presence of sulfur dioxide causes rapid deterioration. Arsenic, boron, cadmium, cerium, chromium, copper, lead, manganese, molybdenum, nickel, silver, tin, titanium, vanadium, zinc and zirconium were chosen for testing to determine if other metals act similarly. They were introduced as nitrates, where possible, in such concentration that 0.5 ccm. per g. of leather gave a concentration of A/50,000 g. of metal per g. of leather, where A is the atomic weight of the metal. Those not introduced as nitrates were vanadium sulfate, arsenious oxide, stannic ammonium chloride, titanium oxide, boric acid and molybdenum oxide. The leather was from a split hide for upholstery leather. Specimens were taken on an 8 by 8 inch Graeco-Latin square pattern to allow accurate comparisons of treatments. To avoid loss of solubles the metal was added by rapid dipping of the leather into the solutions, followed by blotting and weighing, until the desired amount was attained. They were air dried and conditioned at 70 per cent R.H. before exposure to sulfur dixoide in the gas chamber. The samples were exposed 8 weeks. On removal they were conditioned and their buckle-tear strength measured. Three months later the pH of water extract (2 g. leather per 100 ml. of water) of each was taken. The buckle-tear strengths of the leathers treated with lead, silver, manganese, cadmium, molybdenum, cerium, arsenic, nickel, chromium and titanium varied from 150.9 pounds for the first down to 139 pounds for the last. This was not considered significant. The pH of these same leathers varied from the minimum for chromium at 3.98 to the maximum of 4.29 for cadmium. The other five metals caused significant loss in strength. Their buckle-tear loads and pH values are as in the table.

Mean Tearing Loads and pH Values of Water Extracts.

Metal	Tear Load-Pounds	pH
Tin	130.4	3.96
Copper	130.1	3.65
Boron	128.3	4.27
Zirconium	119.6	4.09
Vanadium	72.2	3.44

The pH of water extracts diluted ten times with water was also taken. There is no indication that the 5 elements causing loss of strength did so because of the production of sulfuric acid from the sufur dioxide of the gas chamber. These 5 elements resemble copper more than iron in their action. R.H.T.

Reduction of Chrome-VI Glucose in Sulfuric Acid-Dichromate Solutions. I. Influence of Different Experimental Conditions on the Course of the Reaction. By A. Küntzel and R. Monsheimer. *Das Leder*, **6**, 25 (1955). An investigation of the oxidation of glucose by dichromate (with reduction of the dichromate) during the production of chrome tanning liquors is difficult because many intermediate oxidation products are formed, some of which are bound in the chrome complex. The simplest determinations are of hexavalent chromium (although none of this remains in the final liquor) and of carbon dioxide. A basicity of 33 percent should be found if the reaction follows the equation of Stiasny: $4K_2Cr_2O_7 + 12H_2SO_4 + C_6H_{12}O_6 = 4K_2SO_4 + 8Cr(OH)SO_4 + 6CO_2 + 14H_2O$. If less acid is used so that the calculated value for basicity is 43 percent, the actual basicity will be found to be 33 percent, because of organic acids formed during oxidation of the sugar. A study, based on the determination of hexavalent chromium, was made of the effect of variations of basicity, concentration, and temperature on the reduction of the dichromate. Solutions having different mineral acid basicities were made by adding a 20 percent glucose solution to a solution containing dichromate (equivalent to 250 grams of Cr_2O_3 per liter) and the amount of sulfuric acid required to give the desired basicity in the reduced liquor. After addition of the theoretical amount of glucose, the solution was boiled for two hours, cooled and the unreduced dichromate determined by titrating with N/10 thiosulfate solution. In the basicity from 0 percent to 50 percent only 92-97 percent of the dichromate was reduced; nor was reduction complete when an excess of acid was present. Oxidation was incomplete, not because some of the sugar (glucose) was not oxidized, but because intermediate oxidation products entered a chrome complex and did not oxidize further. The effect of variations in concentration was studied by adding glucose in excess to a mixture of dichromate and sufficient sulfuric acid to give a mineral acid basicity of 43 percent in the reduced liquor. The concentrations were 722, 592, 259 and 94.6 grams of dichromate per liter. The results are presented in curves in which percent reduction is plotted against percent glucose (100 percent glucose is the theoretical amount from the Stiasny equation). The curves were all parallel and were straight lines as long as the amount of sugar was not sufficient for complete reduction of the dichromate. This does not agree with the results of Theis, who reported that in dilute solution oxidation of the glucose proceded only to the formation of oxalic and levulinic acids. Reductions were made at temperatures ranging from —6° to 100°C. by adding 130 percent glucose to a dichromate-acid mixture (43 percent basicity, 253 grams Cr_2O_3 per liter); at lower temperatures the sugar was added slowly (72 to 96 hours). Percentage reduction increased as the temperature increased. Measurement of reduction by volumetric determination of exolved carbon dioxide was made as follows: One component was put in a three-necked flask provided with a stirrer, a burette and a condenser. The second component was added from the burette. The carbon dioxide, after passing through the condenser, was collected over dilute acid in a cylinder. The tray containing the cylinder had an overflow tube through which the displaced acid was led to a graduated cylinder and measured. To displace all carbon dioxide, including that in chromium complexes, it was necessary to strongly acidify the solution in the flask and to boil it. In a standardization with 6.614 grams of potassium carbonate the amount of carbon dioxide found was 1465 milliliters, theory 1481 milliliters, error 1.08 percent. Effect of concentration was studied at 2 levels, 84.3 and 16 grams of chromic oxide per liter (basicity 43 percent). To the boiling solution in the flask a 20 percent sugar solution in 56 percent excess was added in 80 minutes. At the higher concentration the amount of carbon dioxide formed was approximately proportional to the amount of sugar added and very little was liberated after the sugar had all been added. At the lower concentration, evolution of carbon dioxide was slow and much of it was liberated after 80 minutes. When the order of mixing the components was varied the most rapid and complete evolution of carbon dioxide was found when the glucose was added to the dichromate-acid mixture, and the next most rapid evolution when the dichromate-sugar mixture was added to the sulfuric acid. Evolution was

slowest when the acid was added to the dichromate-glucose mixture. Other combinations, — dichromate to glucose-acid, glucose-acid to dichromate, dichromate-acid to glucose, — were intermediate. When the time for addition of the second component was varied from 1 minute to 1 hour. the amount of carbon dioxide liberated was greatest if glucose was added slowly to the dichromate-acid mixture. The opposite was found when the acid was added to the dichromate-glucose mixture; in this case the amount was greatest when the acid was added in 1 minute. In general, because acid catalyzes the reduction process, oxidation is most rapid and complete when the acid is all present at the start, although the temperature and rate of addition of the second component are also factors. Complete oxidation of the sugar is favored by high acidity and high concentration. Slow oxidation is favored by low acidity, dilute solutions, and addition of acid to the dichromate glucose mixture. Slow oxidation of the glucose results in the formation of a greater amount of intermediate products (complex-active, organic acids) and these unite with the reduced chromium to form chrome complexes. I.D.C

The Use in Tanning of Condensation Products of Dicyandiamide and Formaldehyde. By A. Küntzel and E. Quendt. *Das Leder*, **6**, 73 (1955). The term resin tannage has been use to designate methylol compounds of certain nitrogenous bases, namely urea, thiourea, and melamine. The formaldehyde addition compounds of these nitrogen bases are drummed into the hide in aqueous solutions, which also contain free formaldehyde, and are condensed in the hide to water insoluble resin films which coat the hide fibers; at the same time there is a true tannage by the free formaldehyde. Glavas (Oesterr. Lederztg., Festnummer 1954) found that methylol compounds of nitrogen-free substances, for example furfurylalcohol, could act as resin tannins. Miekeley (see this Jour. 49, 459) proposed the use of resin tannins as fillers for chrome leather, but some of his statements regarding dicyandiamid resins appear contradictory. The following work is from a 1952 Doctors thesis by Quendt. Dicyandiamid (Dicy) is made by boiling calcium cyanamide in 2 volumes ofwater for 30 minutes. It crystallizes out on cooling the solution. It is an organic compound with single, double, and triple carbon-nitrogen bonds. From it the trimer, melamine, can be made; it should therefore be a cheaper intermediate than melamine for making a resin tannage. Dicy is neutral but shows amphoteric properties. It forms salts with acids and also with hydroxides of alkalies and alkaline earths although the latter are almost completely hydrolyzed in dilute solutions. The basic character would be expected because of the many nitrogen atoms in the molecule but it is surprising that one hydrogen, presumably the imino hydrogen, is acidic and can be replaced by sodium or potassium to give, for example, potassium dicyandiamid, $H_2N\text{-}\underset{\underset{HN}{|}}{C}\text{-}\underset{\underset{K}{|}}{N}\text{-}C{\equiv}N$ The amphoteric character of dicy explains its high melting point (205°C) and the high temperature coefficient of its solubility in water and alcohol. As the temperature rises from 20° to 100° solubility increases from 3 grams to 88 grams per 100 ml. of water. Dicy forms only one compound, a mono, with methanol. This compound is soluble in water. It does not condense to a resin on acidification, but in neutral or weakly alkaline solution it condenses to a water insoluble compound, however on prolonged heating it decomposes to carbon dioxide and ammonia. The condensation products with formaldehyde vary greatly depending on the relative amounts of the two components and on the condensation time. The following experiments were made by heating on a water bath in a vessel with condenser and stirrer, mixtures of solid dicy and 38% formaldehyde solution. Region 1. —Molar ratio of dicy to formaldehyde 1: 1.5 or below. No resin formed; the mass remained liquid and decomposed on quite long heating with deposition of ammonium carbonate in the condenser. Region 2. —Molar ratio 1: 2 to 1: 3. On long heating the charge changed to a highly viscous, snow-white, resinous mass that remained white and became brittle on cooling. On further hot condensation (with stirring impossible) the mass became solid and glassy. Stirring was impossible after 5 hours with a 1: 2 ratio of after 6

hours with a 1: 2.5 ratio. Region 3. —Molar ratio 1: 3.2 to 3.4. After heating 6-7 hours the resin mass was highly viscous but water-white. If cooled it became opaque white but if removed from the flask and dried in the air it became transparent. On further heating (without stirring) it became solid and glassy. Region 4. —Molar ratio 1: 3.6 to 4.5 Thickening, until stirring was impossible, occured only after heating for 16 hours for the 1: 3.6 ratio, or after 40 hours for the 1: 4.5 ratio. The cooled resin was water-white. If aged in a closed vessel it changed to a solid, insoluble gel; in the air the change to gel was more rapid. With a greater proportion of formaldehyde no gel formed even after heating for 80 hours at which time the experiment was discontinued. In general if the ratio was 3.6 or less the liquid condensation product (after the first 20-30 minutes) formed a white, opaque precipitate or a milky suspension if water was added. Only when the ratio (dicy to formaldehyde) was greater than 1: 3.6 was the condensation product soluble in water. As an example, with a molar ratio of 1: 4, during the first half hour the solution remained clear (A stage; Sellet and Dawson, U.S. Patent 2,567,238) when diluted with water, although if the solution was evaporated in a desiccator the residue was viscous showing that condensation had started. On heating more than 30 minutes the product formed a milky suspension (B stage) when diluted with water, until heating had been continued for about 5 hours more when the product could again be diluted with water without formation of a precipitate (C stage). Solubility then did not change until the material became too thick to stir in about 22 hours. The reason for this solubility behavior is that in the middle pH range the condensation product is isoelectric and therefore insoluble. It becomes water soluble if the pH is either raised or lowered. The insoluble region decreases as the proportion of formaldehyde increases and as the time of condensation increases. For retanning or filling chrome leather the resin must deposit within the hide. Less stable (more easily deposited) products are formed with lower proportions of formaldehyde. Longer times of condensation result in products with larger particle size so that wide variations are possible in particle size and therefore in penetration and sensitivity to deposition. Salting out can be accomplished with sodium chloride, ammonium sulfate or chloride, or sulfuric, hydrochloric, or oxalic acids. If the acid concentration is too high however salting out does not occur probably because the cyanide group is saponified to an acid amide group. Salting out can be combined with pickling (see Dawson, *This Jour.* **47,** 457). The C stage resin gave a moderate precipitate with gelatin-salt solution that was easily removed by shaking. It was obsorbed by hide powder but most of it could be washed out so that its affinity for collagen was too weak to be called a true tanning action. Hide did not tan to a leather-like product with C-stage resin. For retanning, the resin does not coat the fibers but only fills the empty spaces because of its large particle size; it therefore does not change the leather grain as does a vegetable retannage. Dicy resin is too stable to give off formaldehyde so it will not tan and lower tensile strength, however the C stage resin does contain free formaldehyde.

I.D.C.

Quantitative Estimation of Amino Acids by Circular Paper Chromatography. By N. A. N. Rao and T. K. Wadhwani. *J. Indian Inst. Sci.* **37,** 130 (1955). Protein is hydrolyzed with 6*N* HCl and the hydrolysate evaporated to dryness The residue is extracted with isopropyl alcohol and its pH adjusted to 6-7. The nitrogen content of protein and its hydrolysate is then determined. In the meanwhile a suitable aliquot of the extract is spotted, in three separate chromatographic papers, on the circumference of a circle of 1″ radius, drawn at the center of a filter paper of 9″ radius. After drying, each chromatogram is run at 60-60° F. with one of the three solvents (I, butanol, water, ethanol; II, butanol, water, acetic acid; III, butanol, water, acetic acid of three times strength as in II), with the aid of a wick, made by rolling along its length, till the solvent boundary reaches the periphery of the paper. This takes about 16 to 18 hours. The chromatogram is removed, dried, sprayed with ninhydrin in acetone, the latter evaporated, and the paper finally heated at 65° C. for 15 minutes. The colored bands corresponding to each amino acid, except those corresponding to proline and hydroxyproline, are cut out, the color of each band extracted with ethanol saturated with copper sulfate. The color intensity is then measured with a spectrophotometer.

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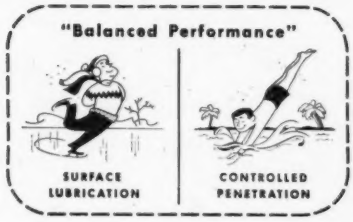

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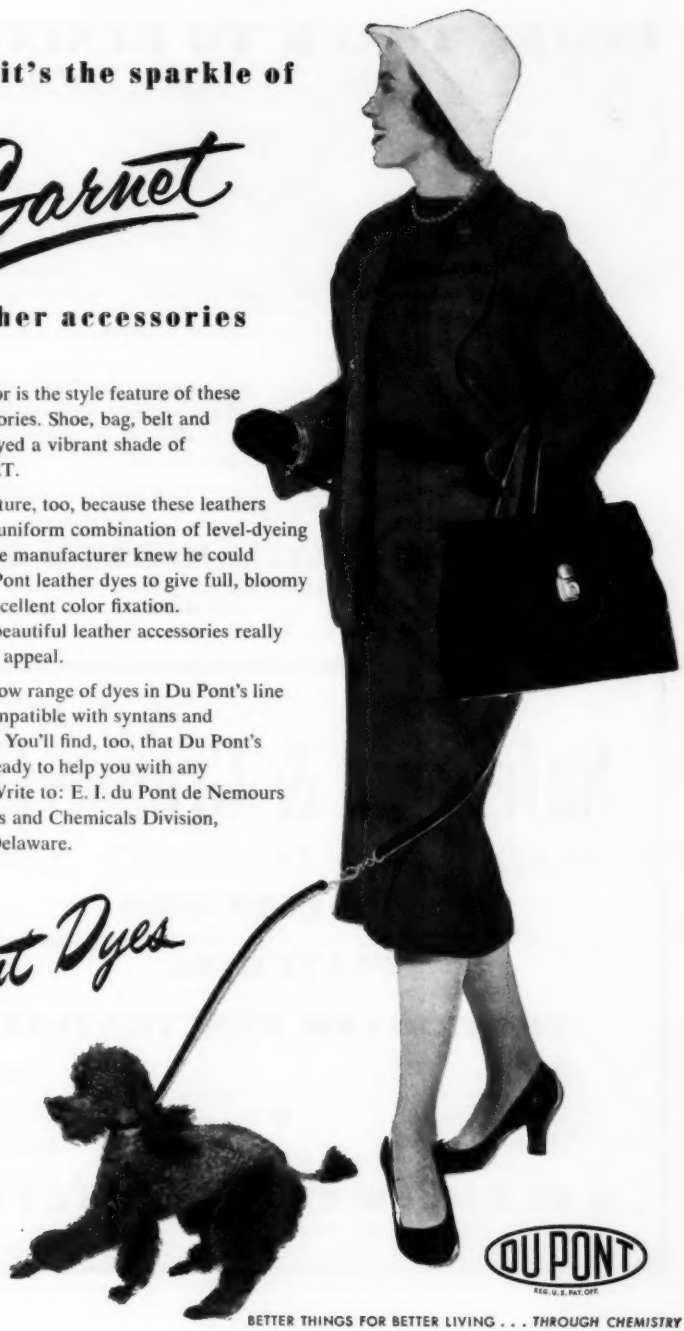

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